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The Dihalides of Group IVB Elements

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The elements of Group IVB (C, Si, Ge, Sn, and Pb) all possess the ground state configuration  $ns^2p^2$ . This configuration suggests that oxidation states of either two or four are especially probable for the elements in the group, and to a greater or lesser extent, both states are observed for each number. There is a continuous increase in the stability of the divalent state with respect to the tetravalent state with increasing atomic number, so that with carbon the (II) - oxidation state is restricted to the very reactive carbenes and to "special" compounds such as isonitriles, whereas (II) is the prevalent state in the inorganic compounds of tin and lead. Two factors probably contribute to this increase in stability of the divalent state. For one, the M-X bond energies generally decrease down the group, with the exception that the bonds between silicon and the most electronegative elements are usually stronger than the corresponding bonds to carbon.<sup>1</sup> Secondly, repulsive interactions between non-bonding and bonding electron pairs are larger for the smaller atom at the top of the group.<sup>2</sup>

There has been some uncertainty as to the relative electronegativities of the various members of Group IVB. The current consensus seems to favor the order  $C > Ge > Si \sim Sn > Pb$ , but the difference in electronegativity between Si and Pb may be small.<sup>3</sup> At any rate, electronegativity differences seem inadequate to explain the monotonic increase of stability of the (II) state as one goes down the group.

The "inert pair" concept has sometimes been advanced to account for the extra stability of atoms or ions which contain a lone pair of s-electrons (e.g.  $Hg^{+1}$  or  $Tl^{+1}$ ); however, this effect does not seem to be particularly

operative in Group IV, since the 3rd ionization potentials are similar for the elements Si through Pb.

The chemistry of the dihalides of the Group IVB elements has developed along several lines. One approach has been to use the dihalides as reactive intermediates in liquid phase studies. For example,  $\text{CCl}_2$  is produced by the alkaline hydrolysis of chloroform; this  $\text{CCl}_2$  can then react with other reagents in the system. A very large amount of work has been done on this type of study and since it is already extensively described in the literature<sup>4</sup> it will only be briefly discussed in this article. The dihalides of Group IVB elements, particularly  $\text{CF}_2$ , are also intermediates in a number of gas phase reactions. Another important approach has been to design experiments that produce the dihalides in conditions that prevent their immediate reaction with other reagents in the system. This has permitted the direct measurement of some of their physical properties and also the determination of some of their descriptive chemistry. It has been principally this technique that has been used in the chemistry department of Rice University, Houston. In this article some of the results obtained using all of these approaches are described although the last technique will be emphasized.

#### A. Difluoromethylene

$\text{CF}_2$  is unique among carbenes because of its high stability and low reactivity. Investigations of the ultraviolet absorption spectrum of  $\text{CF}_2$  have led to estimates of roughly 10 milliseconds to one minute for the half-life of  $\text{CF}_2$  at pressures in the region of one atmosphere. The gas-phase molecule does not react with  $\text{BF}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{CS}_2$  or  $\text{CF}_3\text{I}$  at  $120^\circ\text{C}$ .<sup>5</sup>

The nature of  $\text{CF}_2$  is perhaps best presented in separate sections discussing its preparation, structure and physical properties, reaction chemistry, and reaction kinetics.

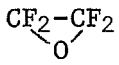
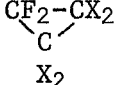
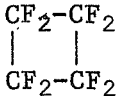
Preparation. The majority of the preparations of  $\text{CF}_2$  reported in the literature involve photolytic or pyrolytic processes. Table I contains a representative list of methods used to produce  $\text{CF}_2$ . Most of the reactions produce the molecule in its singlet ground state, but the reaction of  $\text{O} (^3\text{P})$  atoms with  $\text{C}_2\text{F}_4$  and the decomposition of  $\text{CF}_4$  in a glow discharge appear to produce triplet  $\text{CF}_2$ . In this connection it is interesting to note that the reaction of  $\text{Hg} (^3\text{P})$  atoms did not give rise to triplet  $\text{CF}_2$ ; the authors suggested that the triplet  $\text{C}_2\text{F}_4$  initially formed passes through an excited singlet prior to dissociation.

Structure. The ultraviolet emission spectrum of  $\text{CF}_2$  was first examined by Venkateswarlu<sup>22</sup>, who prepared the molecule by passing an uncondensed transformer discharge through  $\text{CF}_4$ . An extensive band system between 3250 and 2400  $\text{\AA}$  was observed. The similarity of the band system to that of  $\text{NO}_2$  suggested that a non-linear triatomic molecule was responsible for the spectrum. Venkateswarlu identified the band system with the transition  $^1\text{B}_2 \rightarrow ^1\text{A}_1$ .

The ultraviolet absorption bands were examined by Laird, Andrews and Barrow<sup>23</sup> who obtained much the same results as Venkateswarlu although they suggested that the band numbering previously assigned might be incorrect. They demonstrated that the observed system involves the ground state of  $\text{CF}_2$ . Since their equipment design permitted examination of only long-lived species, they estimated that the half-life of  $\text{CF}_2$  is approximately 1 second at a pressure of 1 mm Hg.

Table 1

Methods of Production of  $\text{CF}_2$ 

<u>Starting Material</u>	<u>Products</u>	<u>Multiplicity</u>	<u>Reference</u>
Photolytic methods:			
$\text{CF}_2=\text{CF}_2 \xrightarrow{\text{h}\nu}$	$2\text{CF}_2$	singlet	6
$\text{CF}_2=\text{CF}_2 \xrightarrow[\text{(Hg-sensitized)}]{\text{h}\nu}$	$2\text{CF}_2$	singlet	7
$\text{CF}_2\text{N}_2 \xrightarrow{\text{h}\nu}$	$\text{CF}_2 + \text{N}_2$	singlet	8
$\text{O} (^3\text{P}) + \text{C}_2\text{F}_4 \xrightarrow{\text{h}\nu}$	$\text{CF}_2 + \text{CF}_2\text{O}$	triplet	9
Fluorocarbons $\xrightarrow{\text{h}\nu}$	$\text{CF}_2 + \text{various compounds}$	singlet	10
$\text{ClF}_2\text{COCClF}_2 \xrightarrow{\text{h}\nu}$	$\text{CF}_2 + \text{ClCOCF}_2\text{Cl}$	singlet	11
Pyrolytic methods:			
$\text{CF}_3\text{COCF}_3 \xrightarrow{600^\circ\text{C}}$	$\text{CF}_2 + \text{CF}_3\text{COF}$	singlet	12
$\text{CF}_2-\text{CF}_2 \xrightarrow{120^\circ\text{C}}$ 	$\text{CF}_2 + \text{CF}_2\text{O}$	singlet	13
$\text{CF}_3\text{Sn}(\text{CH}_3)_3 \xrightarrow{150^\circ\text{C}}$	$\text{CF}_2 + \text{FSn}(\text{CH}_3)_3$	singlet	14
$(\text{CF}_3)_3\text{PF}_2 \xrightarrow{120^\circ\text{C}}$	$\text{CF}_2 + (\text{CF}_3)_2\text{PF}_3$	singlet	5
$\text{CF}_2-\text{CX}_2 \xrightarrow{160-200^\circ\text{C}}$ 	$\text{CF}_2 + \text{CX}_2=\text{CX}_2$	singlet	15
Fluorocarbons $\longrightarrow$	$\text{CF}_2 + \text{other products}$		10
Other methods:			
$\text{CF}_4 \xrightarrow{\text{glow discharge}}$	$\text{CF}_2 + \text{several other species}$	triplet	16
$\text{C} + \text{CF}_4 \xrightarrow{2000^\circ\text{C}}$	$\text{CF}_2$	singlet	17
$\text{CHF}_3 \xrightarrow{\text{shock wave}}$	$\text{CF}_2 + \text{HF}$	unknown	18
$\text{CF}_2=\text{CF}_2 \xrightarrow{\text{shock wave}}$	$\text{CF}_2$	unknown	19
$\text{CF}_2-\text{CF}_2 \xrightarrow{\text{r.f. discharge}}$ 	$\text{CF}_2$	unknown	20
$\text{CH}_2 + \text{CF}_2=\text{CF}_2 \longrightarrow$	$\text{CF}_2 + \text{CH}_2=\text{CF}_2$	unknown	21

More recent experiments<sup>24</sup> have resulted in the re-assignment of the band system origin, the extension of spectral measurements to shorter wavelengths, and the correlation of the observed absorption spectra solely with the bending modes of the two states involved. In addition, Simons<sup>25</sup> and Margrave<sup>26</sup> have suggested that the spectra are due to the transition  ${}^1B_1 \leftarrow {}^1A_1$ , rather than  ${}^1B_2 \leftarrow {}^1A_1$ , as originally proposed. Mathews<sup>27</sup> has analyzed the rotational fine structure of the band at  $2540 \text{ \AA}$ , and obtained the following values for molecular parameters: upper state,  $\angle FCF = 134.8^\circ$ ,  $r_{C-F} = 1.30 \text{ \AA}$ ; lower state,  $\angle FCF = 104.9^\circ$ ,  $r_{C-F} = 1.30 \text{ \AA}$ .

The infrared spectrum of matrix-trapped  $CF_2$  (produced by the photolysis of difluorodiazirine,  $CF_2N_2$ ) has been examined<sup>28</sup>. The three fundamental vibrational frequencies were determined to be 668, 1102, and  $122 \text{ cm}^{-1}$ . The intensities of the two stretching fundamentals were sufficiently strong to permit observation of the corresponding absorption of  ${}^{13}CF_2$ , from which the bond angle of  $CF_2$  was calculated to be approximately  $108^\circ$ . The gas-phase infrared spectrum of  $CF_2$  has been observed by Pimental and Herr<sup>29</sup>. Difluorodiazirine was flash-photolyzed and the infrared spectrum of the products was immediately taken with a rapid-scan infrared spectrometer. Absorptions due to  $CF_2$  were seen but the resolution of the instrument was insufficient for determination of the symmetry of the absorptions. The half-life of  $CF_2$  was estimated to be 2.5 m secs.

Powell and Lide<sup>30</sup> observed the microwave spectrum of  $CF_2$  using a fast-flow microwave spectrometer. The  $CF_2$  was prepared by passing a weak r.f. discharge through  $C_2F_3Cl$ ,  $CF_4$  or  $(CF_3)_2CO$ . The absence of fine structure and observable Zeeman shifts provided evidence that the  $CF_2$  was in

the singlet ground state. The bond angle was determined to be  $104.9^\circ$  and the bond length to be  $1.30 \text{ \AA}$ , in complete agreement with Matthews' values (see ref. 27). For comparison, the C-F bond length in  $\text{CF}_4$  is  $1.317 \pm 0.005 \text{ \AA}$ .<sup>31</sup>

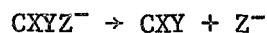
The Heat of Formation of  $\text{CF}_2$ . A number of experimental approaches has been used to determine  $\Delta H_f^\circ(\text{CF}_2)$ . The most common technique involves mass spectrometric measurement of appearance potentials. The earlier appearance potential measurements indicated that  $\Delta H_f^\circ(\text{CF}_2) = -30 \pm 10 \text{ kcal. mole}^{-1}$ ,<sup>32</sup> but it now appears this value is too high. Margrave and co-workers<sup>33</sup> reported a mass spectrometric study of the  $\text{C}_2\text{F}_4/\text{CF}_2$  equilibrium between  $1127\text{--}1244^\circ\text{K}$ . Both second and third-law determinations of the enthalpy of reaction for  $\text{C}_2\text{F}_4 \rightarrow 2\text{CF}_2$  were made, yielding  $-39.3 \pm 3 \text{ kcal. mole}^{-1}$  for  $\Delta H_f^\circ_{298}(\text{CF}_2, \text{g})$ .

Two groups have studied the pyrolysis of  $\text{CF}_2\text{HCl}$  and have calculated  $\Delta H_f^\circ(\text{CF}_2)$  to be  $-43$  and  $-39.1 \text{ kcal. mole}^{-1}$ , respectively.<sup>34</sup> Shock waves were also used to study the formation of  $\text{CF}_2$  from  $\text{C}_2\text{F}_4$  and  $\text{CHF}_3$ ; values of  $\Delta H_f^\circ(\text{CF}_2) = -39.7 \pm 3.0$  and  $-40.2 \pm 4.0 \text{ kcal. mole}^{-1}$  respectively<sup>18,19</sup> were obtained. Other methods that have been used to determine  $\Delta H_f^\circ(\text{CF}_2)$  include the pyrolysis of  $\text{CF}_4$  on graphite<sup>35</sup> and the observation of predissociation in ultraviolet absorption spectra<sup>36</sup>.

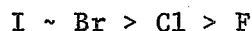
Reaction Chemistry of  $\text{CF}_2$ . The reactions of  $\text{CF}_2$  that have been studied to date fall conveniently into two categories: reaction in solution and reaction in the gas phase. Recently, however, there have also been some investigations of the reactions of matrix-isolated  $\text{CF}_2$ . No attempt will be made in this article to recount the large number of investigations into solution-phase dihalocarbene chemistry; a brief summary of dihalocarbene

solution chemistry will be given in the following section. The interested reader is directed to several reviews of this subject<sup>4</sup>.

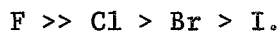
In solution, dihalocarbenes are often produced from the basic hydrolysis of haloforms:



Hine has shown that the relative ability of substituent halogens to enhance trihalo anion formation is



and that halogens facilitate carbene formation in the order



This latter sequence has been attributed to the relative ability of the halogens to supply unshared pairs to the electron-deficient carbon atom, as represented by the hybrids shown below



In the case of difluoromethylene, Hine suggested that formation of the carbene is so favored that dehydrohalogenation occurs in a concerted fashion, with no carbanion intermediate.

Several other methods of generating dihalocarbenes in solution have been reported; the most useful of these appears to be the thermolysis of phenyltrihalomethyl mercury compounds as reported by Seyferth and co-workers<sup>37a</sup>, although other organometallic precursors have also been employed<sup>37b</sup>.



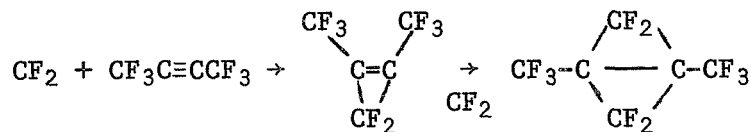
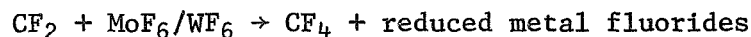
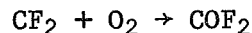
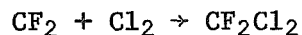
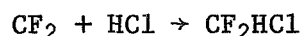
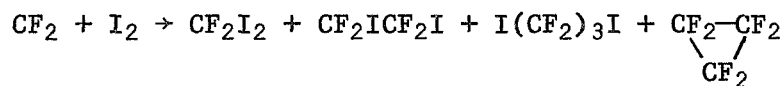
The advantages of this method of carbene synthesis are that reaction can be carried out in neutral solution, and that reaction yields are often dramatically improved. Thus, although reactions of dihalocarbenes generally do not give



rise to products corresponding to single bond insertion, Seyferth has reported insertion of phenyl(trihalomethyl) mercury-generated carbenes into C-H, Si-H, Ge-H, O-H, B-C, Hg-X, Sn-X, Si-Hg, Ge-Hg and Sn-Sn bonds<sup>37</sup>.

Much of the literature regarding dihalocarbenes is concerned with reactions of CX<sub>2</sub> with olefinic substrates to give 1,1-dihalocyclopropane derivatives. These reactions occur with retention of stereospecificity, as expected for singlet carbenes. Dihalocarbenes also exhibit strong electrophilic behavior towards olefins, and will often not react with weakly nucleophilic species if stronger nucleophiles are present.

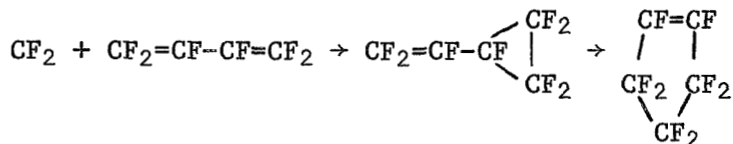
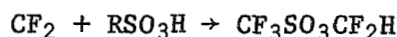
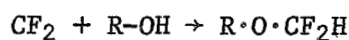
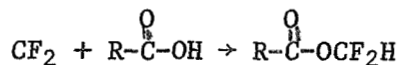
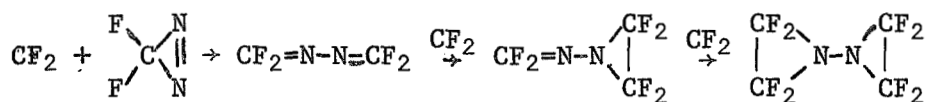
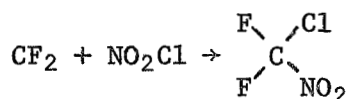
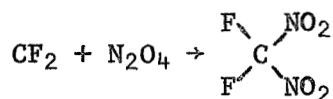
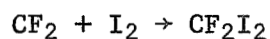
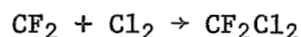
Gas-phase Reactions of CF<sub>2</sub>. In the gas phase, CF<sub>2</sub> is remarkably unreactive as compared to CH<sub>2</sub>. This situation has been dramatically demonstrated by Mahler<sup>5,38</sup>, who did not observe reaction between CF<sub>2</sub> (as produced from the pyrolysis of trifluoromethylfluorophosphoranes at 120°) and BF<sub>3</sub>, H<sub>2</sub>, CO, NF<sub>3</sub>, CS<sub>2</sub>, PF<sub>3</sub>, SO<sub>2</sub>, CF<sub>3</sub>I or N<sub>2</sub>O. Mahler did report the following reactions:



The CF<sub>2</sub>/I<sub>2</sub> reaction is complicated by the fact that I<sub>2</sub> reacts with C<sub>2</sub>F<sub>4</sub> to give CF<sub>2</sub>I-CF<sub>2</sub>I<sup>39</sup>. The HCl reaction is interesting since, as Mahler points

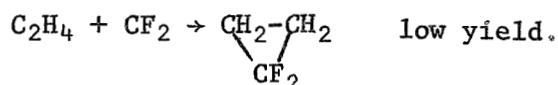
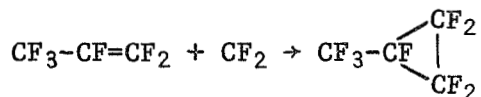
out, it is the reverse of a reaction often used to produce  $\text{CF}_2$ . The reaction of  $\text{CF}_2$  with  $\text{O}_2$  is surprising in light of the many kinetic studies of the reactions of  $\text{CF}_2$  in the presence of  $\text{O}_2$ , to be discussed later.

Mitsch<sup>40</sup> studied the reaction of  $\text{CF}_2$  produced from the photolysis of  $\text{CF}_2\text{N}_2$ , and reported the following reactions

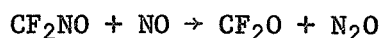
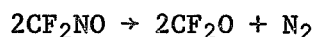
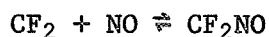


Perfluoro-1,4-pentadiene and perfluoropropene undergo similar reactions.

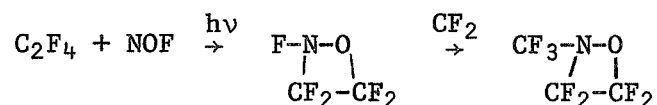
Atkinson and McKeagen<sup>41</sup> reported two similar reactions:



Behind a shock wave  $\text{CF}_2$  reacts with  $\text{NO}$ <sup>42</sup>:



$\text{CF}_2$  also reacts with  $\text{NOF}$ . In this case the  $\text{CF}_2$  used was prepared by the photolysis of  $\text{C}_2\text{F}_4$  and the reaction was complicated by the reaction between  $\text{C}_2\text{F}_4$  and  $\text{NOF}$ .<sup>43</sup>



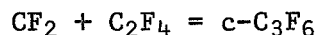
Mastrangelo<sup>20</sup> has reported some interesting work on the reactions of  $\text{CF}_2$  trapped in matrices. A stream of octafluorocyclobutane was passed through a radio frequency discharge and condensed on a liquid nitrogen-cooled cold finger. The resultant deposit was an intense dark blue which persisted until the cold finger warmed to ca.  $95^\circ\text{K}$ . When radical generation times exceeded 15 minutes, however, the blue condensate slowly changed to a red color believed to be associated with  $\text{CF}_3^\cdot$  radicals. On warming, the blue condensate gave rise to  $\text{C}_2\text{F}_4$  and unreacted  $\text{c-C}_4\text{F}_8$ , but no polymeric residue. When chlorine was condensed on the blue deposit before warmup,  $\text{CF}_2\text{Cl}_2$  and  $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ , with smaller amounts of  $\text{CF}_3\text{Cl}$ , were observed in the products. Mastrangelo attributed the blue color to the presence of  $\text{CF}_2$  radicals, and the ensuing red color to the disproportionation of  $\text{CF}_2$  to  $\text{CF}$  and  $\text{CF}_3$ . No determination of the spin state of either the gas-phase or condensed species was reported; in view of the intense color of the condensate, the absence of polymeric radical chains, and the proposed disproportionation of  $\text{CF}_2$  to  $\text{CF}$  and  $\text{CF}_3$ , the presence of triplet  $\text{CF}_2$  seems quite possible.

Milligan and Jacox<sup>44</sup> have recently reported an elegant synthesis of  $\text{CF}_2$  in an argon matrix. Carbon atoms, produced from the photolysis of

cyanogen azide, were allowed to react with molecular fluorine, and the presence of  $\text{CF}_2$  was demonstrated from infrared spectra. Use of radiation effective in photolyzing  $\text{F}_2$  produced  $\text{CF}_3$  from the reaction of the  $\text{CF}_2$  with atomic fluorine.

Kinetic Studies of the Gas-Phase Reactions of  $\text{CF}_2$ . As mentioned above, when gaseous  $\text{CF}_2$  is produced in the presence of substances with which it does not react, the products obtained are tetrafluoroethylene and perfluorocyclopropane<sup>5</sup>. The decay of  $\text{CF}_2$  was originally thought to follow zero-order kinetics (that is, removal of  $\text{CF}_2$  by means of diffusion to the walls of the apparatus)<sup>45,23</sup>. A study of the flash-photolysis of  $\text{C}_2\text{F}_4$  by Dalby<sup>6</sup>, however, showed that  $\text{CF}_2$  decay follows second order kinetics, and a rate constant of  $1.7 \times 10^7$  (liter/mole·sec) at  $25^\circ$  was determined for dimerization of  $\text{CF}_2$  to  $\text{CF}_2=\text{CF}_2$ . Dalby further observed that the rate of disappearance of  $\text{CF}_2$  was independent of the concentration of oxygen,  $\text{C}_2\text{F}_4$  or  $\text{C}_2\text{H}_4$  at pressures as high as 40 cm for the latter two. He was thus able to set an upper limit to the rate constant for the reaction of  $\text{CF}_2$  with these molecules of approximately  $10^4$  liter/mole·sec.

Cohen and Heicklen<sup>46</sup> investigated the mercury-sensitized photolysis of  $\text{C}_2\text{F}_4$  and were able to determine the rate constant for the reaction



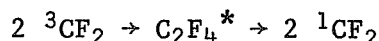
to be  $k_{\text{C}_2\text{F}_4} = 6.4 \times 10^7 \exp(-7500/RT)$  or  $4.5 \times 10^3$  liter/mole·sec at  $25^\circ\text{C}$ .

The ratio of  $k_{\text{C}_2\text{F}_4}$  to the rate constant for dimerization was also found:

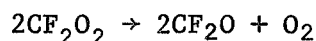
$k_{\text{C}_2\text{F}_4} / k_{\text{dim.}}^{1/2} = 395 \exp(-6700/RT)$  (liter/mole·sec)<sup>1/2</sup>. This ratio has a value of approximately  $5.6 \times 10^{-3}$  at  $25^\circ\text{C}$ . Although this method of  $\text{CF}_2$

production apparently does not yield triplet  $\text{CF}_2$ , the molecule may be

generated via the reaction of ground-state oxygen atoms ( $^3P$ ) with  $C_2F_4$  to yield  $^3CF_2$  and  $CF_2O$ <sup>9,47</sup>. Triplet  $CF_2$ , like the singlet molecule, can add to  $C_2F_4$  to form  $\underline{c}$ - $C_3F_6$ . Triplet  $CF_2$  can also revert to singlet  $CF_2$  through a bimolecular reaction involving an excited  $C_2F_4$  intermediate:



The self-annihilation reaction occurs much faster than addition to  $C_2F_4$ . If molecular oxygen is added to the system,  $^3CF_2$  may then react with  $O_2$  to give  $CF_2O_2$ . This reaction is slightly faster than the combination of  $^3CF_2$ . The  $CF_2O_2$  radicals produced in the reaction with  $O_2$  are removed via



The presence of triplet  $CF_2$  was inferred from the fact that in this system all of the  $CF_2$  species are scavenged by  $O_2$  if the  $O_2$  pressure is greater than 5 torr, coupled with previous observations that the rate of reaction of singlet  $CF_2$  with  $O_2$  is extremely slow<sup>6,7,48</sup>.

Modica and LaGraff<sup>19</sup> have conducted a series of examinations of the production and kinetic aspects of the reactions of  $CF_2$  in shock waves.  $C_2F_4$ , diluted 1:100 with argon, was shocked over the temperature range 1200-1800°K. Ultraviolet absorption of the shocked mixture revealed that dissociation of the  $C_2F_4$  to  $CF_2$  was virtually complete within 1  $\mu$ sec. The dissociation reaction was found to be second order,

$$\frac{1}{2} \frac{d[CF_2]}{dt} = K_{Ar} [C_2F_4] [Ar], \text{ with } K_{Ar} = 7.82 \times 10^{15} T^{-\frac{1}{2}} \exp(-55690/RT) \text{ cc/mole} \cdot \text{sec}$$

The equilibrium constant for the reaction  $C_2F_4 \rightleftharpoons 2CF_2$  was determined to be

$$\log K_c (\text{mole/cc}) = 69432/2.303RT + 4.62$$

The value of  $\Delta H_f^\circ (CF_2)$  calculated from the measured heat of the above reaction agrees well with that obtained by other methods<sup>33,34</sup>, and lends

strength to the assumption that equilibrium conditions prevail in the system.

When oxygen was added to the  $C_2F_4/Ar$  mixture, no reaction with the  $O_2$  was observed below  $1400^\circ K$ . At temperatures above  $1700^\circ K$ , however, the bimolecular oxidation of  $CF_2$  to (initially)  $CO + 2F + O$  was found to occur with

$$K_{ox} = 2.82 \times 10^{10} T^{\frac{1}{2}} \exp (-13280/RT)$$

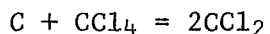
At temperatures in the range  $2600-3700^\circ K$   $CF_2$  itself decomposes to  $CF + F$ , with equilibrium expressed by

$$\log K_c \text{ (mole/cc)} = \frac{-103000 \pm 5700}{2.303 RT} - 0.41 \pm 0.11$$

#### B. Other Carbon Dihalides

Despite the large body of literature discussing the preparation and reaction chemistry of dichloromethylene in solution, very few reports of the isolation of the molecule have appeared. The technique of forming Group IV dihalides from the reduction of the tetrahalide with the metal has proved to be of great utility for production of  $SiX_2$  and  $GeX_2$ , but has not been successful in the case of carbon. Schmeisser and Schröter studied the reaction of  $CCl_4$  with activated charcoal at  $1300^\circ$ , and originally<sup>48a</sup> reported isolation of  $CCl_2$  itself as a mobile, volatile liquid boiling at  $-20^\circ C$ . A subsequent publication<sup>48b</sup> retracted the claim, explaining that an equimolar mixture of dichloroacetylene and chlorine had comprised the "CCl<sub>2</sub>." The paper further stated the  $CCl_4$  was in fact undergoing a surface-catalyzed pyrolysis rather than reaction with the charcoal. Carbon is known to catalyze the decomposition of  $CCl_4$  to  $C + 2Cl_2$ <sup>49</sup>. Schmeisser *et al.* obtained the following products from  $CCl_4$  pyrolysis (yields in parentheses):  $C(35)$ ;  $C_2Cl_2$  (20);  $C_2Cl_4$  (40);  $C_2Cl_6$  (5);  $C_4Cl_6$  (0.1);  $C_6Cl_6$  (0.1). Dichloromethylene was presumably the precursor of the  $C_2Cl_4$ , although the latter

compound could have resulted from disproportionation of  $C_2Cl_6$  to  $Cl_2$  and  $C_2Cl_4$ . Blanchard and LeGoff<sup>50</sup> studied the decomposition of  $CCl_4$  on a tungsten ribbon in the temperature range 1300-2000°K. The  $CCl_4$  vapor, at a pressure of  $10^{-5}$  mm Hg, was made to flow past the ribbon and directly into the ionization source of a mass spectrometer, which was then utilized to analyze the products. Between the temperatures of 1300 and 1600°, the major pyrolysis products were  $CCl_2$  and  $Cl_2$ ; between 1600 and 1900°  $CCl_2$  and  $Cl$  prevailed. When a carburized tungsten ribbon was used virtually identical results were obtained, indicating that the reaction

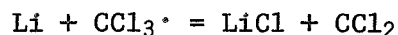


was not important under the existing conditions. The ionization potential of  $CCl_2$  was determined to be  $13.2 \pm 0.2$  eV, and the appearance potentials of the various  $C-Cl_n^+$  ions were used to calculate approximate bond dissociation energies of the corresponding neutral species.

Three groups have recently claimed to have isolated  $CCl_2$  in low-temperature matrices and to have observed the molecule spectroscopically. Milligan and Jacox<sup>51</sup> prepared  $CCl_2$  in a manner analogous to that described for their matrix synthesis of  $CF_2$ . Carbon atoms formed in situ from the photolysis of  $N_3CN$  were allowed to react with  $Cl_2$  in an argon or nitrogen matrix at 14°K. Subsequent to irradiation, two new bands at 721 and 748  $cm^{-1}$  were observed in the infrared spectrum of the matrix. The relative intensity of the bands remained constant under varying conditions. The features disappeared rapidly on warmup of the matrix, with corresponding growth of bands assigned to  $CCl_4$ . Moreover,  $^{13}C$  isotopic studies demonstrated that the compound in question contained only one carbon atom. The above observations were taken as evidence for the existence of  $CCl_2$  as the species in question, and the bands at 721 and 748  $cm^{-1}$  were assigned to the stretching fundamentals

of the molecule. The bond angle for  $\text{CCl}_2$  was estimated to lie in the range  $90\text{--}110^\circ$ . The authors also reported a weak band system between 4400 and  $5600\text{ \AA}$ , with a band spacing of  $305\text{ cm}^{-1}$ , to be associated with  $\text{CCl}_2$ -containing matrices. By analogy with known electronic spectra of  $\text{CF}_2$ , the system was attributed to a transition from the singlet ground state to the first excited state, with an extensive progression in the upper state bending vibration.

Andrews<sup>52</sup> isolated  $\text{CCl}_2$  in an argon matrix by means of the reaction of Li atoms with  $\text{CCl}_4$ .  $\text{CCl}_3\cdot$  radicals are formed from the abstraction of a Cl atom from  $\text{CCl}_4$  by Li, and  $\text{CCl}_2$  is produced from the secondary reaction



The loss of  $\text{CCl}_2$  absorption on matrix warmup was accompanied by the growth of bands attributed to  $\text{C}_2\text{Cl}_4$ . A complete isotopic analysis of the  $\text{CCl}_2$  spectra supported the assignment of the stretching fundamentals as  $\nu_1 = 719.5$  and  $\nu_3 = 745.7\text{ cm}^{-1}$ , in excellent agreement with the work of Milligan and Jacox. The weak  $\nu_2$  (bending) mode was not observed. The bond angle of  $\text{CCl}_2$  was estimated to be  $100^\circ \pm 9^\circ$ , which strongly indicates that the observed species is in the singlet electronic configuration. Stretching force constants were calculated, and  $F_{\text{C-Cl}}$  was found to be lower than the corresponding value for  $\text{CCl}_4$ —a fact which Andrews claims to be evidence for lack of significant pi-bonded contributions to the C-Cl bonds. This result is surprising since doubly-bonded resonance hybrids have long been invoked to explain the stability of dihalocarbenes.

About the same time as the publication of Milligan and Jacox' and Andrews' work, Steudel<sup>53</sup> claimed to have observed the infrared spectrum of  $\text{CCl}_2$  condensed from the pyrolysis (or decomposition in a high-frequency



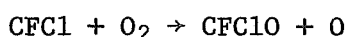
discharge) of several C-Cl compounds.  $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_6$ ,  $\text{CHCl}_3$ , and  $\text{CSCl}_2$  were passed individually through a furnace at  $900^\circ\text{C}$ , and immediately condensed on a KBr window at  $83^\circ\text{K}$ . In each instance, a broad band in the IR spectrum at  $896\text{ cm}^{-1}$  was seen. The absorption diminished in intensity as the matrix was warmed, finally disappearing at  $160\text{--}200^\circ\text{K}$ . Since the pyrolysis products in each case included  $\text{C}_2\text{Cl}_4$ ,  $\text{CCl}_2$  was assumed to be the common intermediate in each reaction.

Although  $\text{CCl}_2$  may well have been an intermediate in the pyrolytic reactions reported by Steudel, it seems clear that the molecule is not responsible for the observed band at  $896\text{ cm}^{-1}$ . Andrews<sup>54</sup> has recently described the infrared spectrum of matrix-isolated  $\text{CCl}_3$ , and located one of the stretching modes ( $\nu_3$ ) at  $898\text{ cm}^{-1}$ . Since the reactions discussed in Steudel's work all produce  $\text{C}_2\text{Cl}_6$  as well as  $\text{C}_2\text{Cl}_4$ , he likely observed the  $\text{CCl}_3$  radical.

The area of gas-phase chemistry of dichloromethylene is as yet largely unexplored. Haszeldine and co-workers<sup>37b</sup> have prepared  $\text{CCl}_2$  from the pyrolysis of  $\text{CCl}_3\text{SiCl}_3$  and  $\text{CCl}_3\text{SiF}_3$ . The  $\text{CCl}_2$  thus produced was observed to react with ethylene and a number of butenes in 85-95% yield, and with  $\text{C}_2\text{Cl}_4$  in 69-85% yield. Addition to cis- or trans-2-butene occurred with retention of stereospecificity. No report of the dimerization of  $\text{CCl}_2$  to  $\text{C}_2\text{Cl}_4$  was given. These preparations belong to the general class of  $\alpha$ -elimination reactions of trihaloalkyl organometallics, several of which were discussed in the section on  $\text{CF}_2$ . In a variation of this type of work Skell and Cholod<sup>55</sup> prepared  $\text{CCl}_2$  in the gas phase by pyrolysing  $\text{CHCl}_3$  at  $1400^\circ\text{K}$ . This pyrolysis was carried out immediately above a solution of olefins and the  $\text{CCl}_2$  reacted with these olefins to give dichlorocyclopropane derivatives. The authors argue that this confirms the fact that free  $\text{CCl}_2$  is

indeed the intermediate in  $\alpha$ -elimination reactions.

Other than some solution chemistry very little indeed is known about  $\text{CBr}_2$  and  $\text{Cl}_2$  or about mixed dihalocarbenes. Tyerman<sup>56</sup> has observed the band spectrum of  $\text{CFCl}$  between 3736-3466  $\text{\AA}$ . Its main feature is a progression of bands with an average spacing of  $386\text{ cm}^{-1}$ . He also observed that, in contrast with  $\text{CF}_2$ ,  $\text{CFCl}$  reacts with  $\text{O}_2$  at room temperature.



### C. Silicon Difluoride

If the gaseous species resulting from passing  $\text{SiF}_4$  over elemental silicon at  $1100\text{--}1400^\circ$  are condensed at temperatures below  $-80^\circ$  and subsequently allowed to warm to room temperature, a waxy, tough white polymer of composition  $(\text{SiF}_2)_n$  is obtained<sup>57</sup>. Mass spectrometric analyses of the gas phase products of the  $\text{Si}/\text{SiF}_4$  reaction indicate that  $\text{SiF}_2$  and  $\text{SiF}_4$  account for over 99% of the species present, with the percentage of  $\text{SiF}_2$  typically near 60%<sup>58</sup>. Gaseous silicon difluoride is extraordinarily stable compared to dihalocarbenes and other silicon dihalides. Its half-life at a pressure of 0.2 mm has been estimated to be 150 seconds<sup>58</sup>. Unlike other Group IV difluorides,  $\text{SiF}_2$  shows no tendency to form gas phase dimers, and is essentially unaffected by the addition of many other gases (except for oxygen, which facilitates formation of  $\text{Si-O-F}$  polymers on the walls of the apparatus).

The low-temperature condensate of  $\text{SiF}_2$  is a yellow-brown paramagnetic solid which remains unchanged when maintained at  $-196^\circ$ . If, however, another substance is co-condensed with the  $\text{SiF}_2$ , the low-temperature species can be made to react—usually on warming. The reaction chemistry thus investigated has proved to be quite extensive, and likely represents the

most comprehensive study of the low-temperature chemistry of a high-temperature molecule. Results of the various examinations of the physical and chemical properties of  $\text{SiF}_2$ , most of which have been conducted in this laboratory, will be discussed in the following sections.

### Gas Phase Spectra

Ultraviolet Spectra. The first direct evidence for the existence of gas phase monomeric silicon difluoride resulted from observation of emission spectra of the molecule in electric discharges through  $\text{SiF}_4$ <sup>59</sup>. The emission band system was subsequently extended<sup>60</sup>; however, both of these investigations are now thought to have resulted in erroneous vibrational numberings. The ultraviolet absorption spectrum was reported by Khanna, Besenbruch and Margrave<sup>61</sup>, who employed the "usual" preparative technique of reducing the tetrafluoride with the metal. They measured 28 absorption bands in the region between 2325 and 2130  $\text{\AA}$ . The most striking feature of the spectrum was the appearance of a series of bands with a periodicity of  $252 \text{ cm}^{-1}$ . This progression was correlated with the bending frequency of the excited state. As was the case of  $\text{CF}_2$ , no direct evidence for excitation of stretching frequencies was obtained. The vibrationless transition is thought to lie at 2266.4  $\text{\AA}$ , and is likely a  ${}^1\text{B}_1 \leftarrow {}^1\text{A}_1$  transition.

Microwave Spectrum. Rao, et al.<sup>62</sup> were able to observe the microwave spectrum of  $\text{SiF}_2$  by generating the molecule from the high-temperature  $\text{Si/SiF}_4$  reaction and pumping the reaction mixture through an absorption cell. The Si-F bond distance and F-Si-F bond angle were calculated to be 1.591  $\text{\AA}$  and  $100^\circ 59'$ , respectively. The bond angle is smaller, and the bond distance longer than one might anticipate, suggesting that bonding involves mainly  $p^2$  hybridization of the silicon orbitals.

Infrared Spectrum. The infrared spectrum of gaseous  $\text{SiF}_2$  has been recorded from 1050 to 400  $\text{cm}^{-1}$ <sup>63</sup>. Two absorption bands, centered at 855 and 872  $\text{cm}^{-1}$ , were assigned to the symmetric ( $\nu_1$ ) and antisymmetric ( $\nu_3$ ) stretching modes, respectively. The assignment was rendered difficult because of the considerable overlap of the two bands. The fundamental bending frequency occurs below the instrumental range of the study, but a value of 345  $\text{cm}^{-1}$  can be determined from the ultraviolet study. The vibrational frequencies were combined with data from a refined microwave study<sup>64</sup> and utilized to calculate force constants and revised thermodynamic functions.

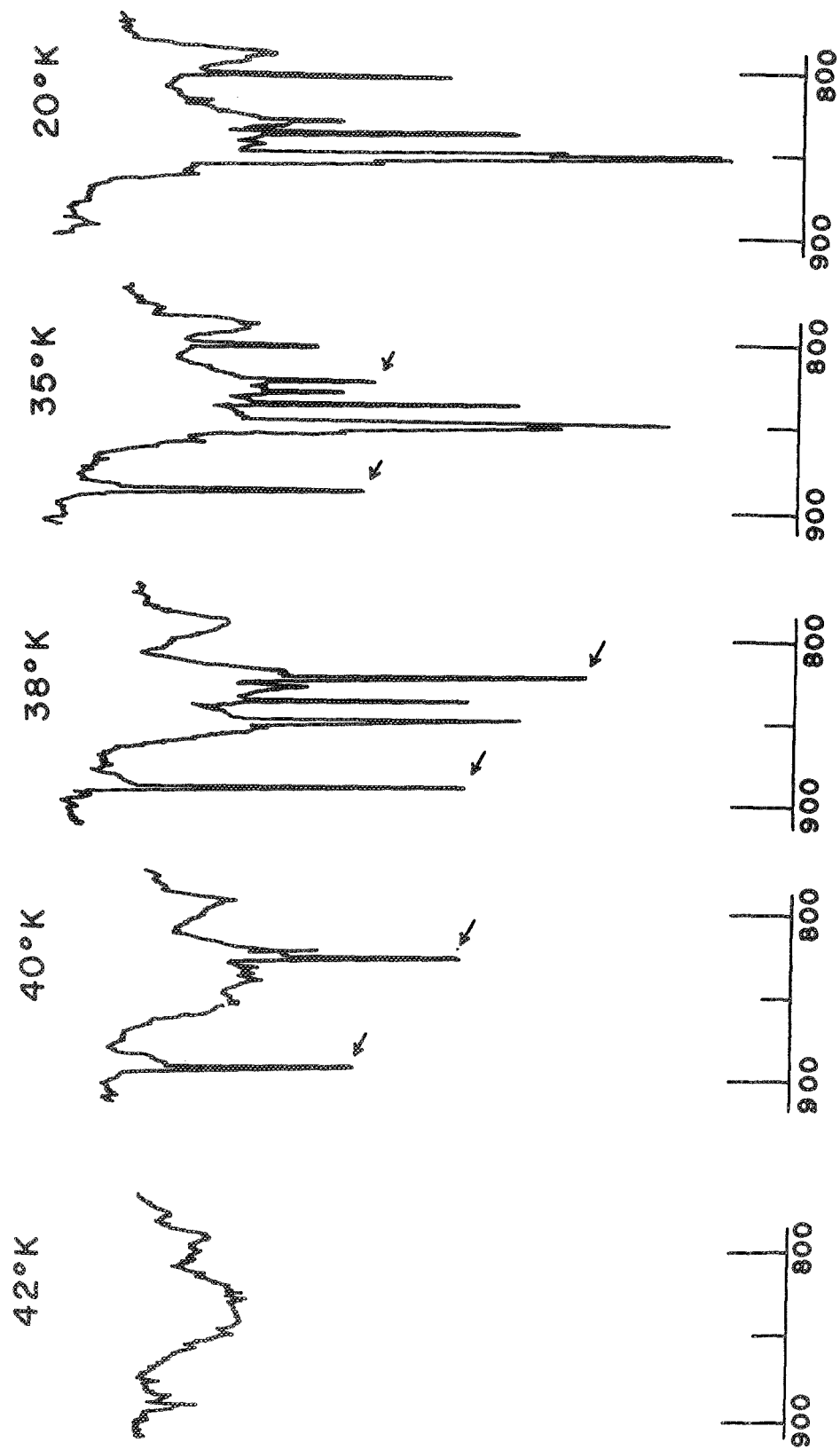
Mass Spectrum. There have been two investigations of the mass spectrum of  $\text{SiF}_2$ . In one experiment<sup>58</sup> the gaseous mixture of silicon fluorides obtained after passing  $\text{SiF}_4$  over a column of Si held at 1150°C was passed into a 5 lt. bulb and thence into a mass spectrometer. Only  $\text{SiF}_4$  and monomeric  $\text{SiF}_2$  were observed; no polymeric species of  $\text{SiF}_2$  were seen. By isolating the 5 lt. bulb containing the  $\text{SiF}_2$  from the furnace and then monitoring the decay of  $\text{SiF}_2$ , it was estimated that  $\text{SiF}_2$  has a half-life of 120 seconds. In a second investigation<sup>65a</sup>  $\text{SiF}_2$  was produced by heating a mixture of Si and  $\text{CaF}_2$  to about 1500°K. From this study the following values were obtained:  $\Delta H_{a,298}^{\text{O}} \text{SiF}_{2,\text{g}} = 12.33 \pm 0.2 \text{ eV}$  and thence  $\Delta H_{f,298}^{\text{O}} \text{SiF}_{2,\text{g}} = -139 \pm 2 \text{ kcal mole}^{-1}$ . This value for the heat of formation of  $\text{SiF}_2$  is not too close to that determined by a transpiration method,  $-148 \pm 4 \text{ kcal mole}^{-1}$ <sup>65b</sup>. The discrepancy probably arises from the interaction between  $\text{SiF}_4$  and  $\text{SiF}_2$  to form  $\text{Si}_x\text{F}_{2x+2}$  at the higher pressures<sup>65c</sup>.

### Studies of SiF<sub>2</sub> Condensate

Infrared Spectrum. Since the reaction chemistry of SiF<sub>2</sub> known to date occurs at low temperatures in the condensed phase rather than in the gas phase, it is naturally of interest to investigate the low-temperature condensate formed from gaseous SiF<sub>2</sub>. The first such investigation was conducted by Bassler, Timms, and Margrave<sup>66</sup>, and involved recording the infrared spectrum of matrix-isolated SiF<sub>2</sub> between the temperatures of 20-40°K. Figure (1) illustrates spectra obtained when a gas-phase SiF<sub>2</sub>/SiF<sub>4</sub> mixture was condensed on a CsI window at 20°K and allowed to warm. One notes that the peak at 811 cm<sup>-1</sup> disappears much faster than the rest of the spectrum as the matrix is warmed. Furthermore, when the furnace-to-window distance is increased to 10 feet, or when nitric oxide is co-condensed with the SiF<sub>2</sub>, the peak is absent altogether. This behavior suggests that the species responsible for the absorption is more reactive than monomeric singlet SiF<sub>2</sub>--perhaps triplet SiF<sub>2</sub>, excited singlet SiF<sub>2</sub>, or SiF<sub>3</sub>. The second spectral feature evident on warmup is the appearance of two new bands at 830 and 892 cm<sup>-1</sup>. These absorptions first appear at about 35°, grow to maximum intensity at 38° (at the expense of bands now known to be due to monomeric SiF<sub>2</sub>), and disappear rapidly on further warming. When the matrix is warmed to 50°K, the spectrum consists of broad bands identical with those of thin layers of (SiF<sub>2</sub>)<sub>n</sub> at room temperature. These facts, especially when viewed in conjunction with the chemical characteristics of SiF<sub>2</sub> condensates, lead to the conclusion that the new bands are due to SiF<sub>2</sub> dimer. The same study also examined some of the earlier

Figure 1 - Infrared spectra of  $\text{SiF}_2$  in argon matrix during warm-up.  
The bands attributed to  $\text{Si}_2\text{F}_4$  are shown by arrows.

FIGURE 1



SiF<sub>2</sub> chemistry by co-condensing potential reactants in the matrix. Most illuminating of these experiments was that involving BF<sub>3</sub>. Previous work had shown that the reaction of SiF<sub>2</sub> with BF<sub>3</sub> (to be discussed in more detail later) leads to a series of compounds BF<sub>2</sub>(SiF<sub>2</sub>)<sub>n</sub>F, with n at least two. When the BF<sub>3</sub>/SiF<sub>2</sub> matrix was allowed to warm, a series of bands not associated with "pure" SiF<sub>2</sub> spectra appeared. The bands began to appear when those associated with (SiF<sub>2</sub>)<sub>2</sub> reach a maximum. Moreover, the new absorptions corresponded closely with those of the gas-phase spectrum of SiF<sub>3</sub>SiF<sub>2</sub>BF<sub>2</sub>, the major product of the SiF<sub>2</sub>/BF<sub>3</sub> reaction on a macroscopic scale.

Two re-examinations of the infrared spectra of matrix-isolated SiF<sub>2</sub> have been reported very recently<sup>67,68</sup>. This work was characterized by improved matrix isolation and by the use of both neon and argon matrices. Hastie, Hauge, and Margrave<sup>67</sup> established the stretching fundamentals in a Ne matrix to lie at 851 (ν<sub>1</sub>) cm<sup>-1</sup> and 865 (ν<sub>3</sub>) cm<sup>-1</sup>, representing a red shift of approximately 8 cm<sup>-1</sup> from the gas phase. A bond angle of 97-102° was calculated from observed isotopic splitting; molecular geometry is thus not greatly perturbed by the matrix environment. Milligan and Jacox<sup>68</sup>, who generated SiF<sub>2</sub> from the vacuum photolysis of SiF<sub>2</sub>H<sub>2</sub> or SiF<sub>2</sub>D<sub>2</sub>, were able to directly observe the bending fundamental of 343 cm<sup>-1</sup> (in an Ar matrix). These authors also measured a series of bands in the ultraviolet which correspond closely to those seen in the gas phase spectrum of SiF<sub>2</sub> (see ref. 61).

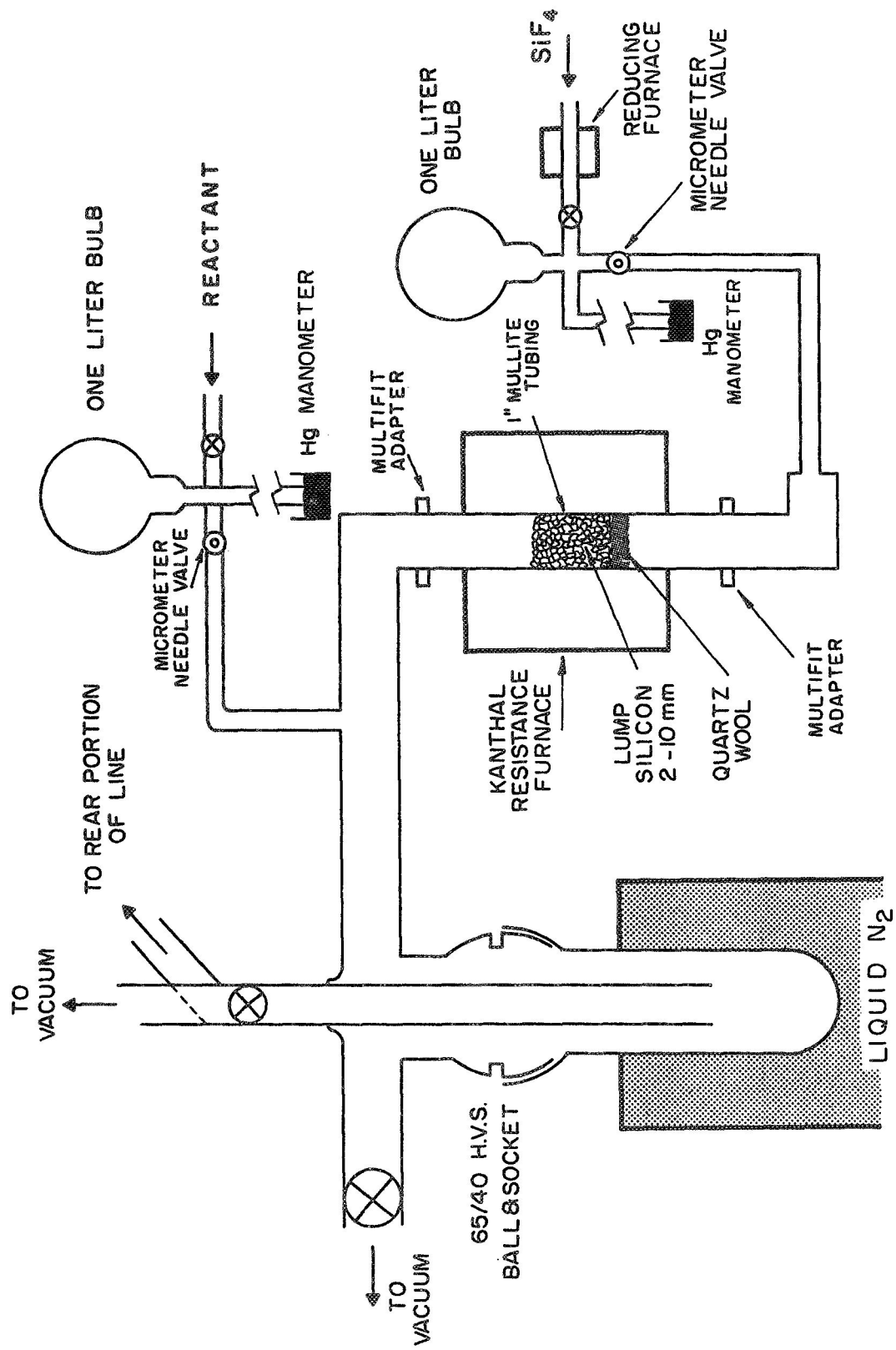


ESR Studies. Both the low-temperature chemistry and the colored appearance of  $\text{SiF}_2$  condensate strongly suggest the presence of radical species containing unpaired electrons. Consequently, an attempt was made in this laboratory<sup>69</sup> to detect an electron spin resonance signal from the condensate. A gaseous  $\text{SiF}_2/\text{SiF}_4$  mixture was condensed on a liquid nitrogen-cooled cold finger in the spectrometer cavity. The condensate generated in this manner gave rise to a broad signal whose intensity was invariant with time as long as the low temperature was maintained. The  $g$  factor for the resonance was  $2.003 \pm 0.002$ , essentially that of a free electron. When the condensate was allowed to warm, the signal decayed rapidly, and could not be regenerated by subsequent cooling--indication that polymerization is irreversible and complete. The nature of the signal is similar to that found upon irradiation of polytetrafluoroethylene<sup>70</sup>.

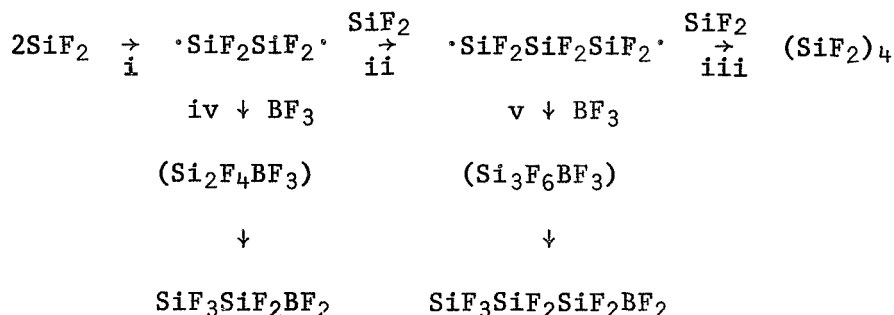
#### Reactions of $\text{SiF}_2$

One of the first reactions of  $\text{SiF}_2$  to be investigated was that with boron trifluoride<sup>71</sup>. The apparatus used to study this reaction is shown in Figure (2); this apparatus is typical of those used in all of the following reactions of  $\text{SiF}_2$ . When  $\text{SiF}_2$  and  $\text{BF}_3$  are co-condensed at  $-196^\circ$ , a green solid results. Warmup of the condensate leads to a number of volatile species, including the new compounds  $\text{SiF}_3\text{SiF}_2\text{BF}_2$  and  $\text{SiF}_3(\text{SiF}_2)_2\text{BF}_2$ . The reaction products each contain at least two silicon atoms, and a gas phase

Figure 2 - Apparatus used to study condensed phase reactions of  $\text{SiF}_2$ .

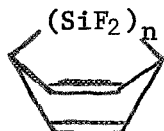


reaction does not occur. These observations lead to the suggestion of the mechanism shown below:



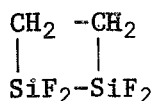
where reactions ii and iii are fast compared to iv and v. In a more recent study<sup>72</sup> a mixture of  $\text{SiF}_2$  and  $\text{SiF}_4$  was reacted with a mixture of  $\text{BF}$  and  $\text{BF}_3$ . The compound  $\text{F}_2\text{Si}(\text{BF}_2)_2$  was isolated from the resultant products. Diboron tetrafluoride was also reacted with  $\text{SiF}_2$  but any new products that were formed were too unstable to be recovered.

The next series of reactions examined involved simple unsaturated and aromatic hydrocarbons and their fluorocarbon analogs. The  $\text{SiF}_2$ /benzene reaction<sup>73</sup> produces a series of compounds of formulae  $\text{C}_6\text{H}_6(\text{SiF}_2)_n$ , with  $n = 2$  to at least 8. Both infrared and ultraviolet spectra indicate the absence of conjugated pi-systems for the  $n = 3$  (highest yield) product. Hydrolysis of the product mixture gives 1,4-cyclohexadiene. These facts, along with the proton nmr spectrum of the compound, permit the conclusion that the products possess the bridged structure shown

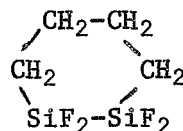


where  $n = 2-8$

The reaction of  $\text{SiF}_2$  with ethylene<sup>74</sup> yields the two cyclic molecules

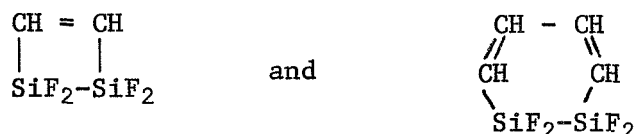


and

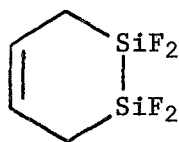


both of which are of quite limited stability. The  $\text{SiF}_2$ /acetylene<sup>75</sup> reaction

proceeds similarly to give

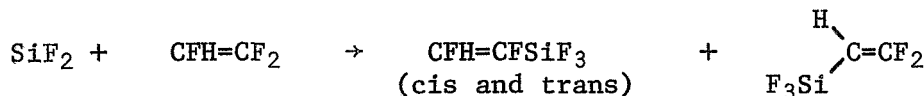
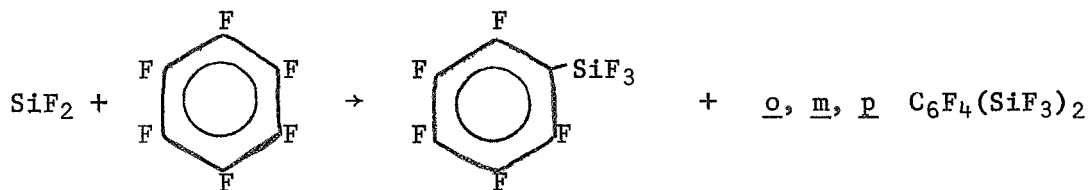


but here the six-membered ring is not isolated and is instead recovered as the rearrangement product,  $\text{HC}\equiv\text{C}-\text{SiF}_2-\text{SiF}_2-\text{CH}=\text{CH}_2$ . Another cyclic compound



was isolated from the reaction of  $\text{SiF}_2$  with butadiene<sup>76</sup>.

The above reactions reinforce the "diradical" mechanism proposed for the  $\text{BF}_3$  reaction. Hexafluorobenzene and the various fluorinated ethylenes<sup>73,74</sup>, however, react quite differently. The products in these reactions formally correspond to C-F bond insertion by an  $\text{SiF}_2$  monomer.

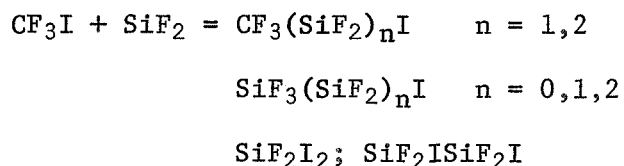


Attack of a C-F bond was shown to be preferential to attack of a C=C bond.

Several quite recent investigations into  $\text{SiF}_2$  chemistry conducted in this laboratory have further indicated the versatility of  $\text{SiF}_2$  as a reactant. Hydrogen sulfide reacts with  $\text{SiF}_2$  to form predominantly  $\text{SiF}_2\text{HSH}$  and  $\text{Si}_2\text{F}_5\text{H}$ <sup>77</sup>. The disilanethiol,  $\text{SiF}_2\text{HSiF}_2\text{SH}$ , expected from addition of  $\text{H}_2\text{S}$  to  $\text{Si}_2\text{F}_4$ , was

obtained in limited yield and was observed to be quite unstable. The  $\text{H}_2\text{S}$  reaction closely paralleled an earlier study of the  $\text{SiF}_2/\text{GeH}_4$  reaction<sup>78</sup> in which the products were the germysilanes  $\text{GeH}_3(\text{SiF}_2)_n\text{H}$ ,  $n = 1-3$ . The  $n = 1$  homolog was the major product and compound stability decreased dramatically with increasing  $n$ .

The reaction of  $\text{SiF}_2$  and iodotrifluoromethane was studied<sup>79</sup> in expectation of obtaining the products corresponding to "addition" of  $\text{CF}_3\text{I}$  to  $(\text{SiF}_2)_n$  species,  $\text{CF}_3(\text{SiF}_2)_n\text{I}$ . The reaction of  $\text{CF}_3\text{I}$  with tetrafluoroethylene has been shown to yield (mainly)  $\text{CF}_3\text{CF}_2\text{CF}_2\text{I}$ <sup>80</sup>. In fact, three separate homologous series of products were characterized:



Excesses of  $\text{CF}_3\text{I}$  in the condensing mixture afforded large yields of  $\text{CF}_3\text{SiF}_2\text{I}$ ; excesses of  $\text{SiF}_2$  resulted in the formation of most or all of the compounds listed above. The  $\text{CF}_3\text{I}$  reaction is of interest as regards reaction mechanisms in  $\text{SiF}_2$  chemistry. As in many other reactions not involving unsaturated reactants, the product obtained in highest yield contained a single silicon atom. Moreover, while each product which contained a  $-\text{CF}_3$  moiety also included an I atom, the converse was not true. Similar behavior was exhibited in the  $\text{H}_2\text{S}$  reaction:  $\text{SiF}_3\text{H}$  and  $\text{Si}_2\text{F}_5\text{H}$  were products;  $\text{SiF}_3\text{SH}$  and  $\text{Si}_2\text{F}_5\text{SH}$  were not. One may make two suggestions from these observations. The first is that diradical species play a major role in  $\text{SiF}_2$  chemistry only when there is no bond of sufficient lability to be attacked by  $\text{SiF}_2$  monomers. (Such reactive bonds include C-F in  $\text{C}_6\text{F}_6$ ; C-I in  $\text{CF}_3\text{I}$ ; and the O-H and S-H bonds in  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ .) Secondly, attack by  $\text{SiF}_2$  or  $(\text{SiF}_2)_n$  often appears to be

stepwise with, in the case of  $\text{CF}_3\text{I}$ , abstraction of an I atom followed by attack on the resultant  $\text{CF}_3$  fragment or abstraction of iodine or fluorine from another molecule.

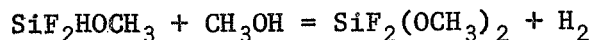
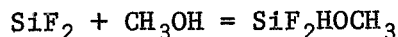
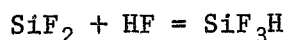
The low-temperature condensate of  $\text{SiF}_2$  and elemental iodine produces only  $\text{SiF}_2\text{I}_2$  and  $\text{SiF}_3\text{I}$ , in the approximate ratio of 3:1, on warming.<sup>79</sup> One must consider the question of whether compounds containing silicon-silicon bonds, such as  $\text{SiF}_3\text{SiF}_2\text{I}$  or  $\text{SiF}_2\text{ISiF}_2\text{I}$ , are formed in the reaction, and suffer Si-Si bond cleavage by unreacted  $\text{I}_2$ . Although some disilanes do undergo fission reactions with  $\text{I}_2$ , the hydrogen analogs of the compounds in question (i.e.,  $\text{Si}_2\text{H}_5\text{I}$  and  $\text{Si}_2\text{H}_4\text{I}_2$ ) react only to give further substitution, eventually yielding  $\text{Si}_2\text{I}_6$ .<sup>81</sup> Moreover,  $\text{Si}_2\text{F}_5\text{I}$  and  $\text{Si}_2\text{F}_4\text{I}_2$ , which were formed in the  $\text{CF}_3\text{I}/\text{SiF}_2$  reaction, exhibited moderate stability in the presence of small amounts of  $\text{I}_2$  generally present in the product mixtures of that reaction, and no evidence of these molecules was found even when large  $\text{SiF}_2/\text{I}_2$  ratios were employed. It seems likely, then, that only  $\text{SiF}_2$  monomers are involved in the  $\text{I}_2$  reaction.

Hydrolysis of a silicon-halogen bond often results in formation of oxygen-containing polymers such as silicones. However the siloxanes  $\text{Si}_2\text{OCl}_6$  and  $\text{Si}_3\text{O}_2\text{Cl}_8$  can be recovered from careful hydrolysis of  $\text{SiCl}_4$ .<sup>82a</sup> The reaction of  $\text{SiF}_4$  with excess water produces fluorosilicic acid and hydrated silica, but if  $\text{SiF}_4$  is passed over wet magnesium sulfate, one obtains the perfluorosiloxanes  $\text{Si}_2\text{OF}_6$  and  $\text{Si}_3\text{O}_2\text{F}_8$ .<sup>82b</sup> The controlled hydrolysis of  $\text{SiF}_2$  might therefore be expected to lead to any of several products. Several oxygen-containing molecules other than water have been observed to react with  $\text{SiF}_2$  to produce homologous series of both linear and cyclic oxyfluorides<sup>83</sup>; alternatively, insertion of an  $\text{SiF}_2$  monomer or telomer into an O-H bond

would result in formation of the silanols  $\text{H}(\text{SiF}_2)_n\text{OH}$ , which would almost certainly be unstable with respect to condensation to siloxanes.

The  $\text{SiF}_2/\text{H}_2\text{O}$  reaction<sup>84</sup> was conducted in a manner designed to minimize the contact of reactants before condensation in the cold trap. Reactions in which the  $\text{SiF}_2/\text{H}_2\text{O}$  ratio varied from 1:1 to 7:1 were conducted, but in all cases the only products not attributable to hydrolysis of  $\text{SiF}_4$  were 1,1',2,2'-tetrafluorodisiloxane,  $\text{SiF}_2\text{HOSiF}_2\text{H}$ , and a voluminous white polymer. No evidence for volatile compounds containing more than two silicon atoms was obtained. The polymer was of interest inasmuch as it, unlike virtually all other  $\text{SiF}_2$  copolymers, was not pyrophoric. Infrared analysis demonstrated the absence of Si-H bonds in the polymer. The structure of the polymer is as yet unknown, but it must differ from the Si-O-F polymers formed in various other  $\text{SiF}_2$  reactions.

The reaction of  $\text{SiF}_2$  with methanol<sup>85</sup> pursued a different course from the water reaction. Here, the reaction products were  $\text{CH}_3\text{OSiF}_3$ ,  $\text{SiF}_3\text{H}$ , and  $(\text{CH}_3\text{O})_2\text{SiF}_2$ . Again, the competing reaction with  $\text{SiF}_4$  represents a complication. In a separate experiment conducted under similar conditions,  $\text{SiF}_4$  was shown to react readily with  $\text{CH}_3\text{OH}$  to form  $\text{CH}_3\text{OSiF}_3 + \text{HF}$ . Further methanolysis of the product to form  $(\text{CH}_3\text{O})_2\text{SiF}_2$ , however, occurred only very slowly. From these and other observations, the authors formulated the following reaction scheme:



Since the Si-H bond has been observed to react readily with methanol<sup>86</sup>, failure to observe  $\text{SiF}_2\text{HOCH}_3$  is not surprising.



Reactions of  $\text{SiF}_2$  with  $\text{NaF}$  and  $\text{LiF}$  have been studied<sup>87</sup>. The alkali fluorides were vaporized from a Knudsen cell and co-condensed with approximately equal amounts of  $\text{SiF}_2$  on a liquid-nitrogen cooled cold finger. The reactions are complicated by gas-phase reactions of  $\text{SiF}_2$  and  $\text{MF}$  and also by the reactions of  $\text{SiF}_4$  with the fluorides. The gas phase  $\text{SiF}_2/\text{MF}$  reactions lead to deposition of  $\text{M}_2\text{SiF}_6$  and elemental silicon on the walls of the apparatus. The low-temperature condensate is a reddish-brown at  $-196^\circ$ , and in all cases decomposes suddenly on warmup. The nature of the low-temperature solid is as yet undetermined.

Conclusions. The utility and versatility of silicon difluoride as a chemical reagent has clearly been demonstrated. Although the region of reactions of  $\text{SiF}_2$  with small (i.e., volatile) organic molecules has been rather well covered, there remain a great number of potentially rewarding reactions with inorganic substances. Rather than dwell on this point, however, the authors would prefer to mention two potential areas for expanding  $\text{SiF}_2$  chemistry.

No direct evidence for the observation of triplet gaseous  $\text{SiF}_2$  exists. If such species could be generated in reasonably high yield (by mercury-sensitized photolysis, for example), their chemistry from both synthetic and kinetic points of view would merit considerable interest. Heicklen and co-workers<sup>46</sup> have successfully conducted similar studies with triplet  $\text{CF}_2$  as generated from the reaction of  $\text{C}_2\text{F}_4$  with ground-state oxygen atoms.

An aspect of Pease's early work with  $\text{SiF}_2$  systems may have significance for the future of  $\text{SiF}_2$  chemistry. In a variation of the usual "matrix-trapping" technique, Pease studied the reaction of  $\text{SiF}_2$  with  $\text{Br}_2$  by passing

the gases through an 8" length of tubing heated to 1200° prior to condensation. Although the same product, SiF<sub>2</sub>Br<sub>2</sub> was collected on warmup of the condensate, none of the usual room-temperature polymer was retained in the reaction trap--indicative of a quantitative gas-phase reaction. The heretofore unknown gaseous chemistry of SiF<sub>2</sub> might well be discovered via a similar approach on a general basis.

#### D. Other Silicon Dihalides

SiCl<sub>2</sub> has long been postulated to be an intermediate in gas-phase pyrolyses of various chlorosilanes<sup>88</sup>, and in such reactions as that of Si and HCl to form SiCl<sub>3</sub>H<sup>89</sup>, or the reduction of perchlorosilanes with H<sub>2</sub><sup>90</sup>. Direct observation of SiCl<sub>2</sub> monomer, or successful attempts to investigate the reaction chemistry of the monomer have, however, been very sparse until quite recently. This situation is in large part due to the fact that the gas-phase lifetimes of the heavier dihalides are several orders of magnitude less than that of SiF<sub>2</sub>. Thus, although equilibrium measurements of the system  $\text{Si} + \text{SiCl}_4 = 2\text{SiCl}_2$ <sup>91</sup> indicate that  $K_p \approx 1$  at 1350°C, techniques similar to those utilized for production of SiF<sub>2</sub> lead to (SiCl<sub>2</sub>)<sub>n</sub> and perchlorosilanes<sup>92</sup>.

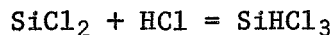
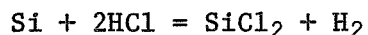
Timms<sup>93</sup> has recently studied SiCl<sub>2</sub> reaction chemistry by employing fast pumping speeds and low (5x10<sup>-6</sup> torr) permanent gas pressures. Under these conditions the SiCl<sub>2</sub>, which is produced from reduction of the tetrahalide with the metal at 1350°, can successfully be condensed on cooled surfaces. Condensation of the equilibrium SiCl<sub>2</sub>/SiCl<sub>4</sub> mixture at liquid nitrogen temperatures gives rise to a brown solid which turns white and evolves perchlorosilanes on warming. Co-condensation of PCl<sub>3</sub>, BCl<sub>3</sub>, or CCl<sub>4</sub> yields

products corresponding to insertion of  $\text{SiCl}_2$  into a M-Cl bond; products containing more than one silicon are not found.  $\text{SiCl}_2$  may behave more similarly to  $\text{SiF}_2$  (that is, diradicals may be important) in its reactions with unsaturated and aromatic compounds; Timms reported that such reactions lead to involatile polymers which incorporate the organic molecule.

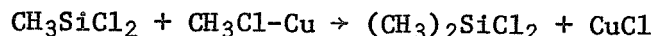
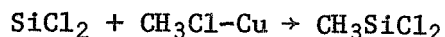
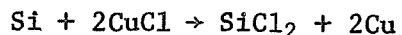
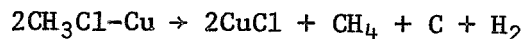
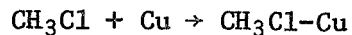
Spectroscopic observations of  $\text{SiCl}_2$  have been reported by Asandi, Karim and Samuel<sup>94</sup> and Milligan and Jacox<sup>95</sup>. The early work of Asandi et al. was concerned with the emission spectra from the products of an electric discharge through  $\text{SiCl}_4$ . The spectrum attributable to  $\text{SiCl}_2$  consisted of a number of features superimposed on a continuous band from 3160 to 3550 Å. The spectral features were used to tentatively assign two of the ground state vibrational fundamentals as 250 and 540  $\text{cm}^{-1}$ . Milligan and Jacox generated  $\text{SiCl}_2$  from the vacuum photolysis of  $\text{SiH}_2\text{Cl}_2$  (or  $\text{SiD}_2\text{Cl}_2$ ) in argon matrices at 14°K. Examination of infrared spectra taken subsequent to photolysis revealed the stretching fundamentals to occur at 502 and 513  $\text{cm}^{-1}$ . It was not possible to assign the symmetries of the two absorptions.

Much of the known high-temperature chemistry of silicon-chlorine compounds is indirectly concerned with  $\text{SiCl}_2$ . The reactions discussed below will serve as examples of those in which the intermediacy of  $\text{SiCl}_2$  is indicated.

The "direct synthesis" of  $\text{SiCl}_3\text{H}$  from Si and HCl has been shown<sup>89</sup> by kinetic studies to proceed via

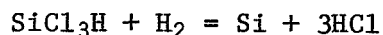
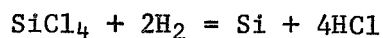


Synthesis of organosilanes from silicon and RCl is facilitated if a silicon-copper alloy is employed<sup>96</sup>. The catalytic action of the copper is due to the formation of CuCl, which then reacts with silicon to form  $\text{SiCl}_2$ :



The existence of  $\text{SiCl}_2$  as an intermediate was indicated from an experiment in which the volatile product of a  $\text{Si/CuCl}$  reaction was allowed to react with  $\text{CH}_3\text{Cl}$  to form methylchlorosilanes.

The high-temperature (1000-2000°K) reactions



were examined by Sirtl and Reuschel<sup>90</sup>. Considerations of silicon yield as a function of temperature and mole fraction of reactants lead to the conclusion that  $\text{SiCl}_2$  is an important reaction intermediate.

The  $\text{SiCl}_4/\text{Si}$  reaction may lead to several different products, depending on reaction conditions. Thus, under conditions of high vacuum and fast pumping,  $\text{SiCl}_2$  may be isolated by rapidly quenching the reaction products. Under less stringent vacuum conditions,  $(\text{SiCl}_2)_n$  is deposited just beyond the hot zone, and the perchlorosilanes  $\text{Si}_n\text{Cl}_{2n+2}$  can be trapped further downstream<sup>92</sup>. If, however,  $\text{SiCl}_4$  is recycled over hot silicon in a closed system<sup>97</sup>, viscous subchlorides of formulae  $\text{Si}_n\text{Cl}_{2n}$  are obtained. The value of  $n$  varies from 12 at 900° to 16 at 1200°. The presumably cyclic compounds were characterized only by standard quantitative analyses; no spectroscopic or other physical data were reported. Bromination of the compounds produced some  $\text{SiCl}_3\text{Br}$ , indicating that at least some open-chain compounds were present.

Since:  $\text{SiCl}_2$  reacts readily with  $\text{SiCl}_4$  under other conditions, it is difficult to explain the apparently quantitative production of  $\text{SiCl}_2$  necessary to form high-molecular weight rings. At any rate, the closed system reaction certainly merits further investigation.

Recent thermochemical data for  $\text{SiCl}_2$  have been reported by Schafer and co-workers<sup>91a</sup>, and by Teichmann and Wolf<sup>91b</sup> from transpiration studies of the  $\text{SiCl}_4/\text{Si}$  system. The heat of formation of the gaseous monomer now seems well established:

$$\Delta H_f^{\circ}(\text{SiCl}_2, \text{g}, 298^{\circ}\text{K}) = -38.2 \pm 1.5 \text{ kcal.}$$

Mass spectrometric investigations of the silicon-chlorine system do not seem to have been made.

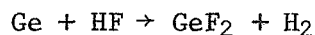
Although for the dibromide and diiodide, the respective  $\text{SiX}_4 + \text{Si} = 2\text{SiX}_2$  equilibria and the reaction chemistry of the  $(\text{SiX}_2)_n$  polymers have been well characterized, the physical and chemical properties of the monomeric dihalides remain virtually unknown. In a preliminary report, Timms<sup>98</sup> related the formation of  $\text{SiBr}_2$  in 90% yield with the apparatus and procedures employed in  $\text{SiCl}_2$  production. The only reaction reported was that with  $\text{BF}_3$ . The sole product was  $\text{BF}_2\text{SiF}_3$ --presumably formed from disproportionation of the expected  $\text{BF}_2\text{SiBr}_2\text{F}$ .

Production of  $\text{SiI}_2$  under similar (i.e., low-pressure high-temperature) conditions is difficult due to the appreciable decomposition of  $\text{SiI}_2$  to Si and I atoms at the temperatures required. Indeed, the diiodide has been utilized for the transportation and deposition of silicon<sup>99</sup>.

#### E. Germanium Difluoride

Germanium difluoride differs dramatically from  $\text{CF}_2$  and  $\text{SiF}_2$  in that it can be isolated as a stable compound at room temperature. Thus, it is surprising that few of its properties have been described.

GeF<sub>2</sub> can be prepared by reducing GeF<sub>4</sub> with Ge at temperatures above 120°C<sup>100</sup>. It can also be prepared by heating germanium powder with anhydrous HF (225°C, 16 hrs)<sup>101</sup>.



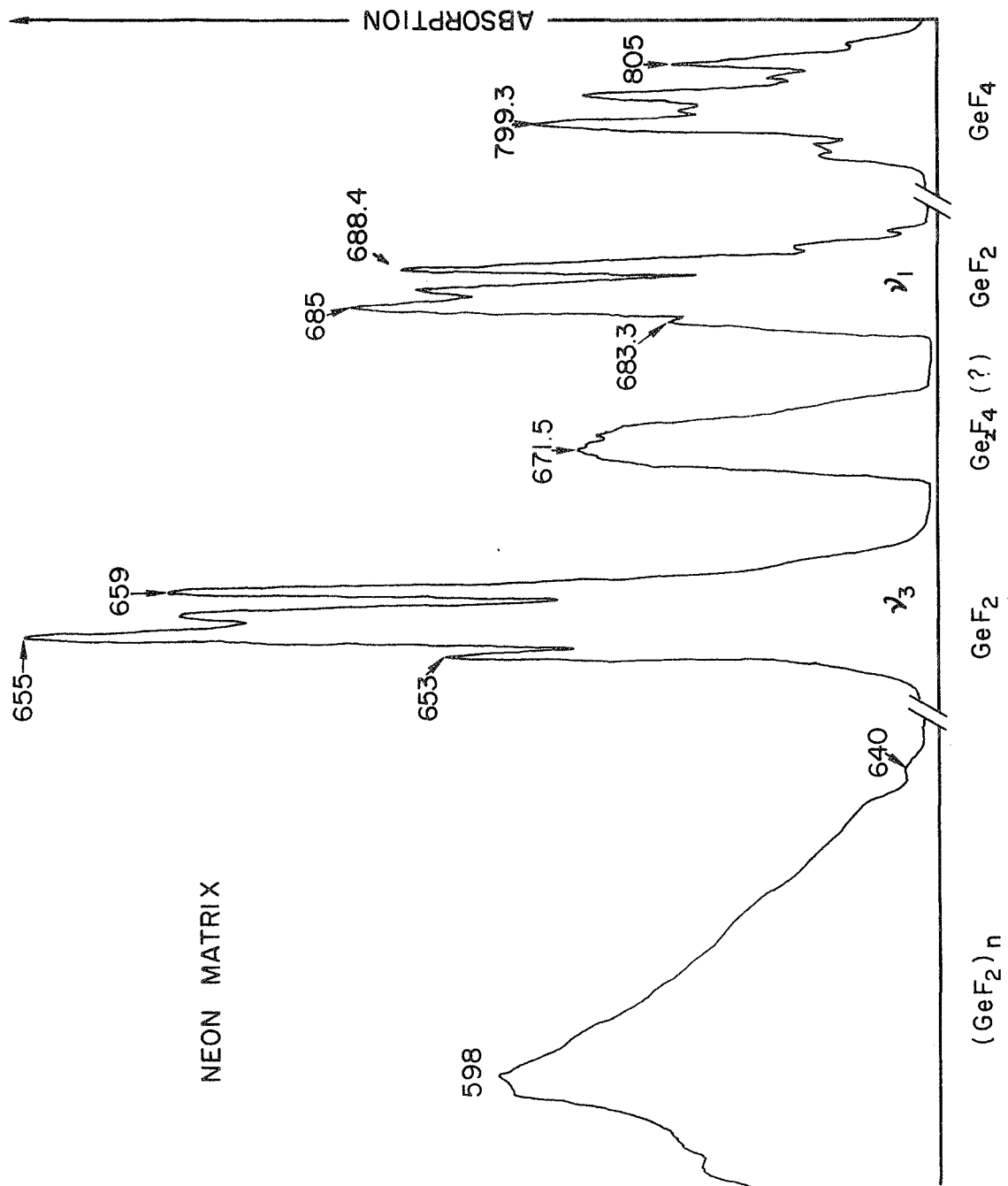
A number of the physical properties of GeF<sub>2</sub> have been measured including its infrared, ultraviolet and mass spectrum. The crystal structure of GeF<sub>2</sub> has also been determined.

The ultraviolet absorption spectrum of GeF<sub>2</sub> has been measured by Hauge, Khanna and Margrave<sup>102</sup>. The spectrum is fairly simple and is probably due to the perpendicular <sup>1</sup>B<sub>1</sub> ← X<sup>1</sup>A<sub>1</sub> transition. All progressions were explained in terms of bending frequencies of the lower and upper electronic states, which are ν<sub>2</sub><sup>''</sup> = 263 cm<sup>-1</sup> and ν<sub>2</sub><sup>'</sup> = 164 cm<sup>-1</sup>. The 0,0,0 - 0,0,0 transition is reported to lie at 2280.1 Å.

The infrared spectrum of GeF<sub>2</sub> has also been reported<sup>103</sup>. Both the gas phase and the matrix-isolated infrared spectra were determined. It was necessary to study the matrix-isolated spectrum for two reasons. First, the examination of the ultraviolet absorption spectrum of GeF<sub>2</sub> indicated that at least ten of the bending states were populated, and second, germanium has five abundant isotopes. These suggested that the gas phase spectrum would be broad and ill defined at the temperatures required to vaporize GeF<sub>2</sub> (150°C). As anticipated the authors found that the gas phase spectrum of GeF<sub>2</sub> did consist of broad absorbances centered at 663 and 676 cm<sup>-1</sup>.

The spectrum of GeF<sub>2</sub> trapped in a neon matrix is shown in Figure 3. The ratio of GeF<sub>2</sub>/rare gas in the matrix was 1:1000. When new matrices were prepared similar spectra were obtained, even when the ratio of diluent was changed or the temperature of deposition was altered. This indicated that

Figure 3: IR absorption spectrum of  $\text{GeF}_2$  matrix isolated in Neon at  $\sim 5^\circ\text{K}$ .





the splitting seen in the spectrum was due to isotope effects and was not due to matrix effects. As can be seen the intensities at the various peaks are in the same ratio as the abundant isotopes of germanium, providing additional evidence that the splitting is due to isotope effects.

One may calculate the bond angle of  $\text{GeF}_2$  from the isotope splitting. If one assumes that the lower frequency absorption is  $\nu_3$ , the bond angle is  $94 \pm 4^\circ$ . If the higher frequency were  $\nu_3$  the bond angle is  $82 \pm 3^\circ$ . Since  $\text{CF}_2$  and  $\text{SiF}_2$  have bond angles of  $104.9^\circ$  and  $100.9^\circ$ , respectively, the value of  $94 \pm 4^\circ$  seems more likely to be the correct value.

There have been several mass spectrometric examinations of  $\text{GeF}_2$ . The first was by Ehlert and Margrave<sup>65a</sup>.  $\text{GeF}_2$  was prepared by heating Ge and  $\text{CaF}_2$ . The appearance potential of  $\text{GeF}_2$  was determined to be  $11.6 \pm 0.3$  eV and the heat of atomization of  $\text{GeF}_2(\text{g})$  to be  $\Delta H_{\text{a},298}^\circ = 16.0 \pm 0.8$  eV, thence  $\Delta H_{\text{f}}^\circ(\text{GeF}_2, \text{c}, 298) = -140 \pm 17$  kcal mole<sup>-1</sup>. The second investigation<sup>104a</sup> has required repetition since it is suspected that possibly the sample used was not pure  $\text{GeF}_2$ .<sup>106</sup> In this more recent examination<sup>104b</sup> the vapor species over pure  $\text{GeF}_2$  was monitored over the temperature range  $70 - 95^\circ\text{C}$ . Only  $\text{GeF}_2$  and  $(\text{GeF}_2)_2$  were found; no  $\text{GeF}_4$  was detected. The thermodynamic data determined from this experiment are listed in Table 2.

The heat of formation of  $\text{GeF}_2$  has very recently been determined by fluorine bomb calorimetry<sup>105</sup>. The value of  $\Delta H_{\text{f}}^\circ(\text{GeF}_2, \text{c}, 298.15^\circ\text{K}) = -157.3 \pm 1.0$  kcal mole<sup>-1</sup> was determined. This is probably the best value currently available.

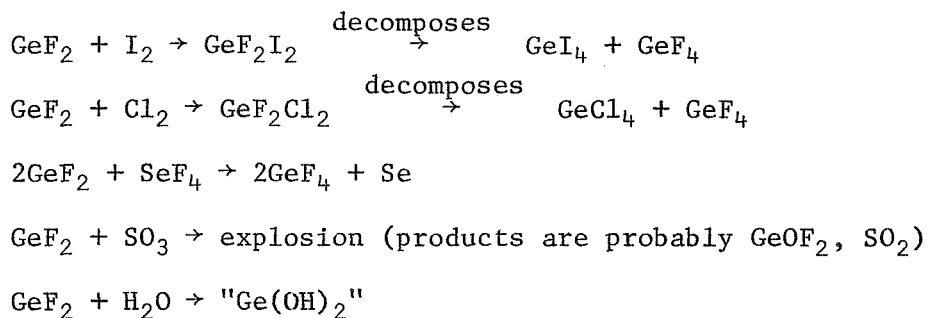
Table 2

Thermodynamic Data from Mass Spectrometer Experiments

Reaction	$\Delta H_{365}^{\circ}$	$\Delta S_{365}^{\circ}$
$\text{GeF}_2(\text{c}) = \text{GeF}_2(\text{g})$	$19.4 \pm 1.0$	$44.7 \pm 2.5$
$2\text{GeF}_2(\text{c}) = (\text{GeF}_2)_2(\text{g})$	$18.3 \pm 2.4$	$36.7 \pm 6.0$

The crystal structure of  $\text{GeF}_2$  was reported by Trotter, Akhtor and Bartlett<sup>107</sup>. They describe  $\text{GeF}_2$  as "a strong fluorine-bridged chain polymer, in which the parallel chains are cross-linked by weak fluorine bridges. The structural unit of the strongly bridged chains is a trigonal pyramid of three fluorine atoms and an apical germanium atom." They found that the Ge-F distances are 1.79, 1.91 and 2.09 Å and the F-Ge-F angles are 85°, 85.6° and 91.6°. The two fluorine atoms at 2.09 Å are equivalent and join the germanium atoms into chains. The F atoms at 1.79 Å are weakly bonded to germanium atoms in neighboring chains whose distance is 2.57 Å. The poor packing of fluorine atoms in this arrangement is due to steric activity of the non-bonding valence electron pair on the germanium. The  $\text{GeF}_4$  group is a distorted trigonal bipyramid with four fluorine atoms and a lone pair (in the equatorial plane) around a germanium atom.

Only a few reactions of  $\text{GeF}_2$  have been reported; however, those currently known indicate that  $\text{GeF}_2$  is a strong reducing reagent.<sup>100b</sup>



Muetterties has described some of the reactions of  $\text{GeF}_2$  in solution<sup>108</sup>. He isolated the salts,  $\text{KGeF}_3$  and  $\text{CsGeF}_3$ , by dissolving  $\text{GeF}_2$  in concentrated solutions of KF and CsF. In solution there must be rapid exchange between  $\text{F}^-$  and  $\text{GeF}_3^-$  since the  $^{19}\text{F}$  nmr signal from a solution containing both species is midway between the signal due to either species alone. If a solution of  $\text{GeF}_2$

is acidified, hydrogen is released. When  $\text{GeF}_2$  is dissolved in dimethyl sulphoxide the complex  $\text{GeF}_2 \cdot \text{OS}(\text{CH}_3)_2$  is formed. No report of bond insertion or additions to multiple bonds by  $\text{GeF}_2$  exist.

#### F. Other Germanium Dihalides

The other germanium dihalides have been known for a very long time. The first reported preparation of  $\text{GeCl}_2$  was later withdrawn; Winkler claimed to have formed  $\text{GeCl}_2$  by reacting heated germanium with  $\text{HCl}$  but the product was actually  $\text{HGeCl}_3$ <sup>109</sup>. Moulton and Miller<sup>110</sup> have shown that  $\text{HGeCl}_3$  is very unstable, and decomposes to  $\text{GeCl}_2$  and  $\text{HCl}$  when distilled at low pressure.  $\text{GeCl}_2$  can be prepared by passing  $\text{GeCl}_4$  over  $\text{Ge}$  at  $350^\circ\text{C}$ <sup>111</sup>. It is also formed by the action of  $\text{AgCl}$  on  $\text{Ge}$ <sup>112</sup> and by the action of  $\text{Cl}_2$  on  $\text{Ge}$  at  $650^\circ\text{C}$ <sup>113</sup>. When  $\text{GeCl}_4$  is reduced by hydrogen, germanium subchlorides of limiting composition  $\text{GeCl}_{0.9}$  are formed. When these subchlorides are distilled under vacuum at  $210^\circ$ ,  $\text{GeCl}_2$  can be isolated.<sup>114</sup>

$\text{GeBr}_2$  and  $\text{GeI}_2$  are much easier to prepare than the difluoride or dichloride.  $\text{GeBr}_2$  can be prepared by reducing  $\text{HGeBr}_3$  with  $\text{Zn}$ , or by the vacuum distillation of  $\text{HGeBr}_3$ .<sup>115</sup>  $\text{GeI}_2$  can be very easily prepared by precipitation from  $\text{Ge}^{2+}$  solutions.<sup>116</sup> It can also be prepared by the action of  $\text{HI}$  on  $\text{GeS}$ .<sup>117</sup>

Although  $\text{GeF}_2$  has been examined by a variety of spectroscopic techniques the other dihalides have not been examined in such detail.

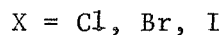
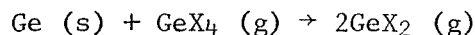
The chemiluminescent emission spectrum of  $\text{GeCl}_2$  was obtained by burning  $\text{GeCl}_4$  in potassium vapor using a diffusion flame technique.<sup>118</sup> The spectrum consisted of a series of closely spaced diffuse bands in the region  $4900\text{--}4100 \text{ \AA}$  with an underlying continuum. The bands resemble those of  $\text{SnCl}_2$ .

These results were taken to indicate that  $\text{GeCl}_2$  is non-linear in the gas phase. If the diffuse nature of the bands is due to predissociation, then the dissociation energy of the  $\text{ClGe-Cl}$  bond is less than 64 kcal.

Both the absorption and the emission spectra of  $\text{GeCl}_2$  were observed by Hastie, Hauge and Margrave<sup>119</sup>.  $\text{GeCl}_2$  was produced either by vaporization from liquid  $\text{GeCl}_2$  or by the reduction of  $\text{GeCl}_4$  with Ge. Absorption occurred between 3301-3140 Å. The transition is probably  $X^1A_1 \rightarrow ^1B_1$ , as is observed for  $\text{CF}_2$ ,  $\text{SiF}_2$  and  $\text{GeF}_2$ . Bands in the spectrum were interpreted in terms of progressions in the bending frequencies of the lower and upper states. The ground state bending frequency is  $162 \text{ cm}^{-1}$  and that of the upper state is  $95 \text{ cm}^{-1}$ .

A microwave discharge through  $\text{GeCl}_4$  vapor at low pressure produced a continuous emission from 3125 to 3341 Å, the same range as that observed in the absorption spectrum of  $\text{GeCl}_2$ .

The thermodynamics of the reactions



have been studied by a number of workers using weight loss methods, static vapor pressure measurements and mass spectrometric techniques. The mass spectrometric investigation showed that  $\text{GeCl}_2$  and  $\text{GeBr}_2$  do not form polymers in the gas phase in contrast with the behavior of  $\text{GeF}_2$ . The numerical results of these various investigations are summarized in Table 3<sup>120</sup>.

Reactions of Germanium Dihalides. Due to its ease of preparation,  $\text{GeI}_2$  possesses the best characterized reaction chemistry of the dihalides of germanium.

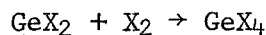
Table 3

Heats of Formation and Atomization of Gaseous Germanium

Dihalides, and Stabilities of Ge-X Bonds, kcal mole<sup>-1</sup>

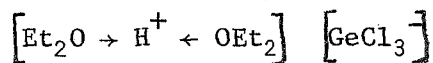
Molecule	$\Delta H_{\text{f},298}^{\circ}$	$\Delta H_{\text{atoms}}^{\circ}$	$\bar{E}(\text{Ge-X})$
GeF <sub>2</sub>	$-136.9 \pm 2^{104\text{b},105}$	$266.3 \pm 2^{104\text{a},105}$	$133.2 \pm 1^{104\text{a},105}$
GeCl <sub>2</sub>	$-42 \pm 1^{120,121}$	$188 \pm 5^{120}$	$94 \pm 2^{120}$
GeBr <sub>2</sub>	$-13 \pm 1^{120}$	$164 \pm 5^{120}$	$82 \pm 2^{120}$
GeI <sub>2</sub>	$13 \pm 2^{123}$	$142 \pm 5^{123}$	$71 \pm 2^{123}$

GeCl<sub>2</sub>, GeBr<sub>2</sub> and GeI<sub>2</sub> all undergo the following reactions:

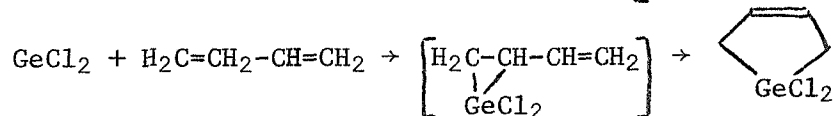
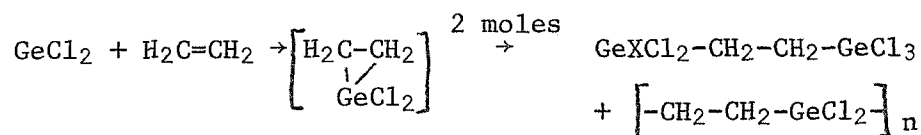
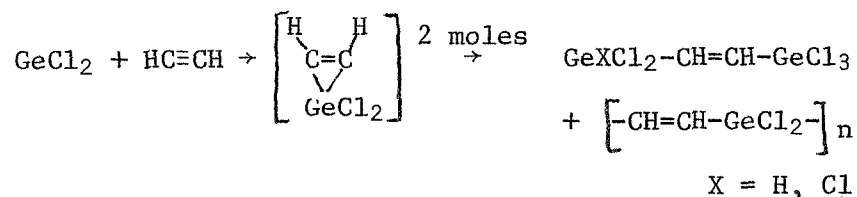
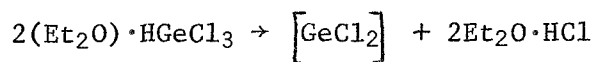


GeCl<sub>2</sub> and GeBr<sub>2</sub> hydrolyze to give "Ge(OH)<sub>2</sub>". GeCl<sub>2</sub> begins to decompose at 75°C, and reacts with H<sub>2</sub>S to give GeS.<sup>124</sup>

Just as CX<sub>2</sub> is formed in solution by the basic hydrolysis of CHX<sub>3</sub>, so can GeX<sub>2</sub> be formed from HGeX<sub>3</sub> in solution. For example, when HGeCl<sub>3</sub> is dissolved in ether it forms the complex 2(Et<sub>2</sub>O)HGeCl<sub>3</sub> which is thought to have the ionic structure

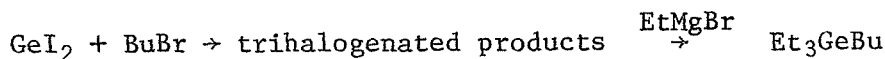
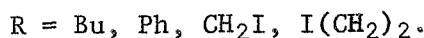


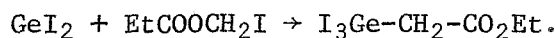
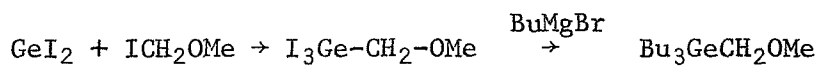
and thus it readily forms GeCl<sub>2</sub>. Typical reactions of the complex are



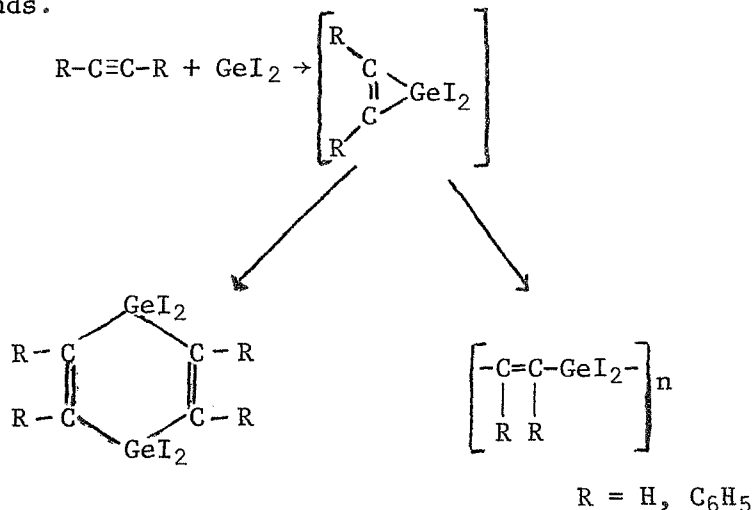
GeBr<sub>2</sub> is observed to undergo similar reactions<sup>124</sup>. No direct reaction was observed between carbonyl compounds and germanium dihalides<sup>125</sup>.

The reactions of GeI<sub>2</sub> have received more attention. GeI<sub>2</sub> will react with a carbon halogen bond.<sup>126</sup>

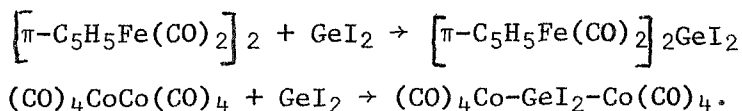




Most of these reactions were carried out in sealed tubes.  $\text{GeI}_2$  also reacts with multiple bonds.<sup>127</sup>

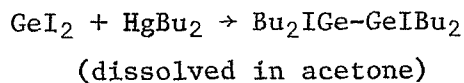
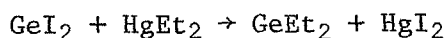


$\text{GeI}_2$  inserts into metal-metal bonds,<sup>128,129</sup>



Similar reactions have been observed for  $\text{GeCl}_2$ <sup>130</sup>. The halide atoms in these compounds are very labile and are easily changed for groups such as -Me, -OCH<sub>3</sub>, -SC<sub>2</sub>H<sub>5</sub>, -NCS, and -OCOCH<sub>3</sub> or other halides<sup>128,130</sup>.

$\text{GeI}_2$  also reacts with organo-mercury compounds.<sup>131</sup>



$\text{GeI}_2$  is also of considerable importance in the transport and purification of germanium.



## G. Tin and Lead Dihalides

The dihalides of tin and lead are so very well known that it is unnecessary to summarize the extensive chemical knowledge of these compounds. The chemistry of divalent tin and lead has been reviewed several times recently.<sup>132</sup> A few points that are relevant to the material already discussed will be made.

The ultraviolet absorption spectra of gaseous  $\text{SnF}_2$ ,  $\text{SnCl}_2$ ,  $\text{PbF}_2$  and  $\text{PbCl}_2$  have all been recently reported. For  $\text{SnF}_2$  a weak absorption with a regular banded structure was seen at around  $2425 \text{ \AA}$ . The bending frequency of the ground electronic state is  $180 \text{ cm}^{-1}$  and for the excited state is  $120 \text{ cm}^{-1}$ . For  $\text{PbF}_2$  no discrete band system was observed; a plot of the bending frequencies of the other Group IVB difluorides against the reciprocal of their internuclear separations enabled  $\nu_2''$  to be estimated as  $145 \text{ cm}^{-1}$  and  $\nu_2'$   $105 \text{ cm}^{-1}$ . For  $\text{SnF}_2$  and  $\text{PbF}_2$  the  $0,0,0 - 0,0,0$  transitions are estimated to occur at  $40,741$  and  $40,560 \text{ cm}^{-1}$ , respectively.<sup>133</sup>

In the ultraviolet  $\text{SnCl}_2$  showed a continuous absorption with a maximum intensity at about  $21,044 \text{ cm}^{-1}$  ( $3220 \text{ \AA}$ ). The absence of discrete bands is probably due to overlapping of closely spaced diffuse bands. For  $\text{PbCl}_2$  three regions of continuous absorption were observed. These had maximum intensities at  $3600$ ,  $3200$  and below  $2916 \text{ \AA}$ . The  $\text{SnCl}_2$  and  $\text{PbCl}_2$  spectra were interpreted as being due to  $^1A_1 \rightarrow ^1B_1$  transitions.<sup>119</sup>

The mass spectra of the vapors over hot  $\text{SnF}_2$  and  $\text{PbF}_2$  were also examined recently.<sup>134</sup>  $\text{SnF}_2$  undergoes some polymerization. Species found over molten  $\text{SnF}_2$  at  $616^\circ\text{K}$  were  $\text{SnF}_2$  79.5%,  $\text{Sn}_2\text{F}_4$  20.5%, and  $\text{Sn}_3\text{F}_6$  0.027%. No dimers were found over  $\text{PbF}_2$ ; this was probably due to the ready decomposition of

these dimers into  $\text{PbF}_4$  and  $\text{Pb}$ . The heats of dimerization for all of the Group IVB difluorides are listed in Table 4.<sup>135</sup> In the same study a number of the thermodynamic functions of the fluorides of tin and lead were measured using Knudsen cell effusion techniques.<sup>134</sup> These values do not agree very well with previously available data. This area has recently been surveyed and interested readers should refer to this survey.<sup>136</sup>

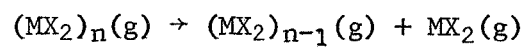
### Conclusions

A varied and productive chemistry is now established for most of the Group IV dihalides. By combining high temperature and low temperature techniques, one may now isolate and observe molecular parameters, as well as physical and chemical properties for  $\text{AX}_2$ -species. The  $\text{CX}_2$  (carbenes) and  $\text{SiX}_2$  (silylenes) molecules have a rich chemistry and provide new and unique opportunities for organic and organo-metallic syntheses.

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Table 4

Heats of Dimerization of Group IVb Difluorides (kcal mole<sup>-1</sup>)

<u>Molecule</u>	<u>n = 2</u>
CF <sub>2</sub>	76.3 ± 3
SiF <sub>2</sub>	—
GeF <sub>2</sub>	18.3 ± 3
SnF <sub>2</sub>	39 ± 2
PbF <sub>2</sub>	—

## REFERENCES

1. T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press Inc., New York, 2nd ed., 1958.
2. M. C. Day and J. Selbin, "Theoretical Inorganic Chemistry," Reinhold, New York, p 212-13, 1962.
3. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Wiley and Sons, 2nd ed., New York, p 456, 1966; A. L. Allred and E. G. Rochow, J. Inorg. Nucl. Chem., 5, 264 (1958); L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, 3rd ed., p 126 (1959); R. T. Sanderson, "Inorganic Chemistry," Reinhold, New York, p 78 (1967).
4. J. Hine, "Divalent Carbon," The Ronald Press Co., New York, 1964; W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, 1964; W. E. Parham and E. E. Schweizerm, Org. Reactions, 13, 55 (1963); E. Chinoporos, Chem. Rev., 63, 235 (1963).
5. W. Mahler, Inorg. Chem., 2, 230 (1963); R. G. Carvell, R. C. Dobbie and W. J. R. Tyerman, Canad. J. Chem., 45, 2849 (1967).
6. F. W. Dalby, J. Chem. Phys., 41, 2297 (1964).
7. J. Heicklen, V. Knight and S. Greene, J. Chem. Phys., 42, 221 (1965).
8. R. A. Mitsch, J. Heterocyclic Chem., 1, 59 (1964).
9. T. Johnston and J. Heicklen, J. Chem. Phys., 47, 475 (1967).
10. Apparently most fluorocarbons form  $\text{CF}_2$  on photolysis, pyrolysis or under the influence of an electric discharge. For a summary of the compounds used and the processes involved for producing  $\text{CF}_2$  in this way see: J. P. Simons and A. J. Yarwood, Nature, 192, 943 (1961); J. Heicklen, N. Cohen and D. Saunders, J. Phys. Chem., 69, 1774 (1965).

11. J. P. Simons and A. J. Yarwood, *Nature*, 187, 316 (1960).
12. W. Batey and A. B. Trenwith, *J. Chem. Soc.*, 1961, 1388.
13. M. Lenzi and A. Mele, *J. Chem. Phys.*, 43, 1974 (1965).
14. H. C. Clark and C. J. Willis, *J. Am. Chem. Soc.*, 82, 1888 (1960).
15. J. M. Birchall, R. N. Haszeldine and D. W. Roberts, *Chem. Comm.*,  
1967, 287. B. Atkinson and D. McKeagan, *Chem. Comm.*, 1966, 189.
16. N. Cohen and H. Heicklen, Aerospace Corp. Report TDR-469 (5250-40)-2,  
Nov. 20, 1964.
17. J. L. Margrave and K. Wieland, *J. Chem. Phys.*, 21, 1552 (1953); L. S.  
Nelson and N. A. Kuebler, *J. Chem. Phys.*, 37, 47 (1962).
18. A. P. Modica and J. E. LaGraff, *J. Chem. Phys.*, 44, 3375 (1966).
19. A. P. Modica and J. E. LaGraff, *J. Chem. Phys.*, 43, 3383 (1965);  
44, 1585 (1966), 45, 4729 (1966).
20. S. V. R. Mastrangelo, *J. Am. Chem. Soc.*, 84, 1122 (1962).
21. N. C. Craig, T. Hu and P. H. Martyn, *J. Phys. Chem.*, 72, 2234 (1968).
22. P. Venkateswarlu, *Phys. Rev.*, 77, 676 (1950).
23. R. K. Laird, E. B. Andrews and R. F. Barrow, *Trans. Faraday Soc.*,  
46, 803 (1959).
24. D. E. Mann and B. A. Thrush, *J. Chem. Phys.*, 33, 1732 (1960); A. M.  
Bass and D. E. Mann, *J. Chem. Phys.*, 36, 3501 (1962); J. P.  
Simons, *J. Chem. Soc.*, 1965, 5406; B. A. Thrush and J. J. Zwolenik,  
*Trans. Faraday Soc.*, 59, 582 (1963).
25. J. P. Simons, *J. Chem. Soc.*, 1965, 5406.
26. V. M. Khanna, G. Besenbruch and J. L. Margrave, *J. Chem. Phys.*, 46,  
2310 (1967).
27. C. W. Matthews, *J. Chem. Phys.*, 45, 1068 (1966).
28. D. E. Milligan, D. E. Mann, M. E. Jacox and R. A. Mitsch, *J. Chem.*  
*Phys.*, 41, 1199 (1964).

29. K. C. Herr and G. C. Pimentel, Appl. Opt., 4, 25 (1965).
30. F. X. Powell and D. A. Lide, Jr., J. Chem. Phys., 45, 1067 (1966).
31. C. W. W. Hofman and R. L. Livingston, J. Chem. Phys., 21, 565 (1953).
32. J. L. Margrave, J. Chem. Phys., 31, 1432 (1954).
33. K. F. Zmbov, O. M. Uy and J. L. Margrave, J. Am. Chem. Soc., 90, 5090 (1968).
34. J. W. Edwards and P. A. Small, Nature, 202, 1329 (1964); F. Gozzo and C. R. Patrick, Nature, 202, 80 (1964).
35. M. W. Farlow, U. S. Patent 2, 709, 142 (May 21st, 1955).
36. B. A. Thrush and J. J. Zwolenik, Trans. Faraday, Soc., 59, 582 (1963).
37. a) D. Sayferth, F. M. Armbrach, Jr. and B. Schneider, J. Am. Chem. Soc., 91, 1954 (1969) and references herein.  
b) W. T. Beran, R. N. Haszeldine and J. C. Young, Chem. and Ind., 1961, 789.
38. W. Mahler, J. Am. Chem. Soc., 84, 4600 (1962); 90, 523 (1963).
39. M. S. Roasch, U. S. Patent 2,424,667 July 29, 1947.
40. R. A. Mitsch, J. Heterocyclic Chem., 1, 233 (1964); J. Heterocyclic Chem., 1, 271 (1964); R. A. Mitsch and E. W. Neuvar, J. Phys. Chem., 70, 546 (1966); R. A. Mitsch, E. W. Neuvar and P. H. Ogden, J. Heterocyclic Chem., 4, 389 (1967); R. A. Mitsch and J. E. Robertson, J. Heterocyclic Chem., 2, 152 (1965).
41. B. Atkinson and D. McKeagan, Chem. Comm., 1966, 189.
42. A. P. Modica, J. Chem. Phys., 46, 3663 (1967).
43. S. Andreades, Chem. Ind. (London), 1962, 732.
44. D. E. Milligan and M. E. Jacox, J. Chem. Phys., 48, 2265 (1968).
45. J. P. Simons and A. J. Yarwood, Nature, 187, 316 (1960).
46. N. Cohen and J. Heicklen, J. Chem. Phys., 43, 871 (1965).

47. N. Cohen and J. Heicklen, J. Phys. Chem., 70, 3082 (1966); J. Heicklen and V. Knight, J. Phys. Chem., 70, 3893 (1966).
48. a) M. Schmeisser and H. Schröter, Angew. Chem., 72, 349 (1960);  
b) M. Schmeisser, H. Schröter, H. Schilder, J. Massonne and F. Roskopf, Ber., 95, 1648 (1962).
49. C. G. Fink and C. F. Bonilla, J. Phys. Chem., 37, 1135 (1933).
50. L. P. Blanchard and P. Le Goff, Canad. J. Chem., 35, 89 (1957).
51. D. E. Milligan and M. E. Jacox, J. Chem. Phys., 47, 703 (1967).
52. L. Andrews, J. Chem. Phys., 48, 979 (1968).
53. R. Steudel, Tetrahedron Lett., 1967, 1845.
54. L. Andrews, J. Chem. Phys., 48, 972 (1968).
55. P. S. Skell and M. S. Cholod, J. Am. Chem. Soc., 91, 6035 (1969).
56. W. J. R. Tyerman, Chem. Comm., 1968, 392.
57. D. C. Pease, U. S. Patent 2,840,588, 24 June, 1958.
58. P. L. Timms, R. A. Kent, T. C. Ehlert and J. L. Margrave, J. Am. Chem. Soc., 87, 2824 (1965).
59. J. W. C. Johns, G. W. Chantry and R. F. Barrow, Trans. Faraday, Soc., 54, 1589 (1958).
60. D. R. Rao and P. Venkateswarlu, J. Mol. Spectroscopy, 7, 287 (1961).
61. V. M. Khanna, G. Besenbruch and J. L. Margrave, J. Chem. Phys., 46, 2310 (1960).
62. V. M. Rao, R. F. Curl, P. L. Timms and J. L. Margrave, J. Chem. Phys., 43, 2557 (1965).
63. V. M. Khanna, R. Hauge, R. F. Curl, Jr., and J. L. Margrave, J. Chem. Phys., 47, 5031 (1967).
64. V. M. Rao and R. F. Curl, J. Chem. Phys., 45, 2032 (1966).

65. a) T. C. Ehlert and J. L. Margrave, J. Chem. Phys., 41, 1066 (1964);
- b) J. L. Margrave, A. S. Kana'an and D. C. Pease, J. Phys. Chem., 66, 1200 (1962).
- c) A. S. Kana'an and J. L. Margrave, Inorg. Chem., 3, 1037 (1964).
66. J. M. Bassler, P. L. Timms and J. L. Margrave, Inorg. Chem., 5, 729 (1966).
67. J. W. Hastie, R. H. Hauge and J. L. Margrave, J. Am. Chem. Soc., 91, 2536 (1969).
68. D. E. Milligan and M. E. Jacox, J. Chem. Phys., 49, 4269 (1968).
69. J. C. Thompson, H. P. Hopkins and J. L. Margrave, J. Am. Chem. Soc., 90, 901 (1968).
70. E. E. Schneider, Disc. Faraday Soc., 19, 158 (1955); M. A. Bruk, A. D'Abkin and P. M. Khomlkovskil, Dok. Akad. Nauk. SSSR, 149, 1322 (1963).
71. P. L. Timms, T. C. Ehlert, J. L. Margrave, F. E. Brinckman, T. C. Farrar and T. D. Coyle, J. Am. Chem. Soc., 87, 3819 (1965).  
J. L. Margrave and P. L. Timms, U. S. Patent No. 3,379,512 (1968).
72. R. W. Kirk and P. L. Timms, J. Am. Chem. Soc., 91, 6315 (1969).
73. P. L. Timms, D. D. Stump, R. A. Kent, and J. L. Margrave, J. Am. Chem. Soc., 88, 940 (1966); J. L. Margrave and P. L. Timms, U. S. Patent No. 3,485,862 (1969).
74. J. C. Thompson, J. L. Margrave, and P. L. Timms, Chem. Comm., 1966, 566.
75. J. C. Thompson, J. L. Margrave, P. L. Timms and C. S. Liu, unpublished results.
76. J. C. Thompson and J. L. Margrave, Inorg. Chem., 9, in press (1970).



77. K. G. Sharp and J. L. Margrave, *Inorg. Chem.*, 8, 2655, (1969).
78. D. Solan and P. L. Timms, *Inorg. Chem.*, 7, 2157 (1968).
79. J. L. Margrave, K. G. Sharp and P. W. Wilson, *J. Inorg. Nucl. Chem.*, in press.
80. R. N. Haszeldine, *J. Chem. Soc.*, 1949, 2856, also 1963, 374.
81. E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, New York, 1963, p 91.
82. a) J. Goubeau and R. Warncke, *Z. Anorg. Chem.*, 259, 109 (1949);  
b) M. Chaigneau, *Compt. Rend.*, 266, 1053 (1968).
83. J. L. Margrave, K. G. Sharp and P. W. Wilson, unpublished results.
84. J. L. Margrave, K. G. Sharp and P. W. Wilson, *J. Am. Chem. Soc.*, 92, 1530 (1970).
85. J. L. Margrave, K. G. Sharp and P. W. Wilson, *Inorg. Nucl. Chem. Letters*, 5, 995 (1969).
86. W. S. Miller, J. S. Peake and W. H. Nebergall, *J. Am. Chem. Soc.*, 79, 5604 (1957).
87. T. W. Harbaugh and J. L. Margrave, unpublished results, (1968).
88. K. Wieland and M. Heise, *Angew. Chem.*, 63, 438 (1951); R. Schwarz *et. al.*, *Chem. Ber.*, 80, 444 (1947).
89. J. Joklik and V. Bazant, *Collect. Czech. Chem. Comm.*, 29, 603 (1964).
90. E. Sirtl and K. Reuschel, *Z. Anorg. Allgem. Chem.*, 332, 113 (1964).
91. a) H. Schafer, H. Bruderreck and B. Morcher, *Z. Anorg. Allgem. Chem.*, 352, 122 (1967);  
b) R. Teichmann and E. Wolf, *Z. Anorg. Allgem. Chem.*, 347, 145 (1966).
92. M. Schmeisser and P. Voss, *Z. Anorg. Allgem. Chem.*, 334, 50 (1964).
93. P. L. Timms, *Inorg. Chem.*, 7, 387 (1968).
94. R. Asundi, M. Karim and R. Samuel, *Proc. Phys. Soc. (London)*, 50, 581 (1938).

95. D. E. Milligan and M. E. Jacox, J. Chem. Phys., 49, 1938 (1968).
96. S. Golubtsov, K. Andrianov, R. Turetskaya, Z. Belikova, I. Trofinova and K. Morozov, Doklady Akad. Nauk SSSR, 151, 1329 (1963).
97. P. Schenk and H. Bloching, Z. Anorg. Allgem. Chem., 334, 57 (1964).
98. P. L. Timms, Abstract of 154th ACS National Meeting.
99. M. Schmeisser and K. Friederich, Angew. Chem., 76, 782 (1964);  
H. Schäfer, German Patent 966,471, August 8, 1957.
100. a) L. M. Dennis and A. W. Laubengayer, Z. Physik Chem., 130, 520 (1927);  
b) N. Bartlett and K. C. Yu, Can. J. Chem., 39, 80 (1961).
101. E. L. Muetterties and J. E. Castle, J. Inorg. Nucl. Chem., 18, 148 (1964).
102. R. Hauge, V. M. Khanna and J. L. Margrave, J. Mol. Spec., 27, 143 (1968).
103. J. W. Hastie, R. Hauge, and J. L. Margrave, J. Phys. Chem., 72, 4492 (1968).
104. a) K. F. Zmbov, J. W. Hastie, R. Hauge and J. L. Margrave, Inorg. Chem., 7, 608 (1968).  
b) G. P. Adams, R. P. Steiger, J. L. Margrave and P. W. Wilson, unpublished results.
105. G. P. Adams, J. L. Margrave and P. W. Wilson, unpublished results.
106. Apparently  $\text{GeF}_2$  reacts with  $\text{GeF}_4$  to form either a complex or a new compound. Possibly Zmbov et al used this new compound instead of  $\text{GeF}_2$  since they prepared their  $\text{GeF}_2$  sample in an excess of  $\text{GeF}_4$ . This reaction is being investigated.
107. J. Trotter, M. Akhtar and N. Bartlett, J. Chem. Soc. (A), 1966, 30.
108. E. L. Muetterties, Inorg. Chem., 1, 342 (1962).
109. J. Winkler, J. prakt Chem., 142, 222 (1886); 144, 188 (1887).
110. C. W. Moulton and J. G. Miller, J. Am. Chem. Soc., 78, 2702 (1956).
111. L. M. Dennis and H. L. Hunter, J. Am. Chem. Soc., 51, 1151 (1929).

112. K. H. Lieser, H. Elias and H. W. Kohlschutter, Z. Anorg. Allgem. Chem., 313, 199 (1961).
113. H. R. Harner and D. S. Trahin, U. S. Patent 2,767,052.
114. R. Schwarz and E. Baronetzky, Naturwissenschaften, 39, 256 (1952).
115. F. M. Brewer and L. M. Dennis, J. Phys. Chem., 31, 1526 (1927).
116. L. S. Foster, Inorg. Synthesis, 3, 63.
117. E. A. Flood, L. S. Foster, E. W. Pietrusza, Inorg. Synthesis, 2, 106.
118. A. Tewarson and H. B. Plamer, J. Mol. Spectry, 22, 117 (1967).
119. J. W. Hastie, R. H. Hauge and J. L. Margrave, J. Mol. Spectry, 29, 152 (1969).
120. O. M. Uy, D. W. Muenow and J. L. Margrave, Trans. Faraday Soc. 65, 1296 (1969) and references herein.
121. T. O. Sedgwick, J. Electrochem Soc., 112, 496 (1965).
122. R. C. Feber, U. S. A. E. C. Rept. LA-3164 (1965).
123. F. Jona, R. F. Lever and H. R. Wendt, J. Electrochem Soc., 111, 413 (1964); D. F. Evans and R. E. Richards, J. Chem. Soc., 1292 (1952).
124. Various of these reactions are reviewed by O. M. Nefedov and M. N. Manakov, Angew Chem. internat. Edit., 5, pp 1027-9 (1964).
125. S. P. Kolesnikov, S. L. Perlmutter and O. M. Nefedov, Doklady Akad. Nauk SSSR, 180, 112 (1968).
126. M. Lesbre, P. Mazerolles and G. Manuel, Compt. Rend., 257, 2303 (1963).
127. M. E. Volpin, Y. D. Koreschkov, V. G. Dulova, and D. N. Kursanov, Tetrahedron, 18, 107 (1962); F. Johnson, R. S. Gohlke and W.A. Nasutavicus, J. Organometallic Chem., 3, 233 (1965).
128. N. Flitcroft, D. A. Harbourne, I. Paul, P. M. Tucker and F. G. A. Stone, J. Chem. Soc. (A), 1966, 1130.

129. D. J. Patmore and W. R. G. Graham, *Inorg. Chem.*, 5, 1405 (1966).
130. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova and F. S. Denisov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 142.
131. G. Jacobs, *Compt Rend.*, 238, 1825 (1954); L. I. Emelyanova, V. N. Vinogradova, L. G. Makarova and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1962, 53.
132. For a recent review see J. D. Donaldson, "Progress in Inorganic Chemistry", Ed. F. A. Cotton, 8, pp. 287-356, Interscience, New York, 1967.
133. R. H. Hauge, J. W. Hastie and J. L. Margrave, *J. Phys. Chem.*, 72, 3510 (1968).
134. K. Zmbov, J. W. Hastie and J. L. Margrave, *Trans. Faraday Soc.* 64, 861  
13 (1968).
135. K. Zmbov, J. W. Hastie and J. L. Margrave, *High Temperature Technology* p 345, Butterworths; London, 1969.
136. G. P. Adams, J. L. Margrave, R. P. Steiger and P. W. Wilson, submitted to *J. Chem. Thermodynamics*, 1970.